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Date: May 2, 1972

RESEARCH PROJECT INITIATION

Project Title: Chemistry of Carbanions

Project No.: G-33-648

Project Director: Dr. Erling Grovenstein, Jr.

Sponsor: National Science Foundation

Agreement Period: From May 1, 1972 until October 31, 1973 *

* 12 month budget period plus 6 months to fulfill all closeout requirements.

Type Agreement: Grant No. GP-33367X

Amount: \$28,000 NSF Funds (G-33-648)
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\$32,890 Total

Reports Required: Annual Letter Technical
Final Technical (Due only if grant is not renewed)

Contact Person(s): Administrative

Mr. W. W. Bolton
Grants Officer
National Science Foundation
Washington, D. C. 20550

Technical

Dr. Donald A. Speer, Director
Chemical Dynamics Program
Chemistry Section
National Science Foundation
Washington, D. C. 20550

This project is a continuation of G-33-620.

Assigned to: School of Chemistry

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GEORGIA INSTITUTE OF TECHNOLOGY
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Date: May 19, 1976

Project Title: "Chemistry of Carbanions"

Project No: G-33-648

Project Director: Dr. ~~Donald A. Speer~~

Erling Grovenstein, Jr.

Sponsor: National Science Foundation

Effective Termination Date: 4/30/76

Clearance of Accounting Charges: 4/30/76

Grant/Contract Closeout Actions Remaining:

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TO: Dr. Donald A. Speer
Program Director for Chemical Dynamics
National Science Foundation
Washington, D. C. 20550

FROM: Dr. Erling Grovenstein, Jr.
Principal Investigator
School of Chemistry
Georgia Institute of Technology

SUBJECT: Technical Report upon "Chemistry of Carbanions"
NSF Grant No. GP-33367X
For Period of May 1, 1972-August 31, 1972

Abstract. - While 4-chloro-1-p-biphenyl-1,1-diphenylbutane reacts with lithium metal in THF in -70° to give 4-p-biphenyl-4,4-diphenylbutyllithium (I) containing up to some 50% of the product of 1,4-migration of p-biphenyl (*i.e.*, 4-p-biphenyl-1,1-diphenylbutyllithium, II), reaction of this chloride with excess lithium biphenyl under appropriate conditions gives I containing only a few percent of II. Although organolithium compound I does not undergo detectable thermal rearrangement to II after several hours in THF at -75° , an almost instantaneous rearrangement occurs upon addition of excess potassium t-butoxide to I at this temperature.

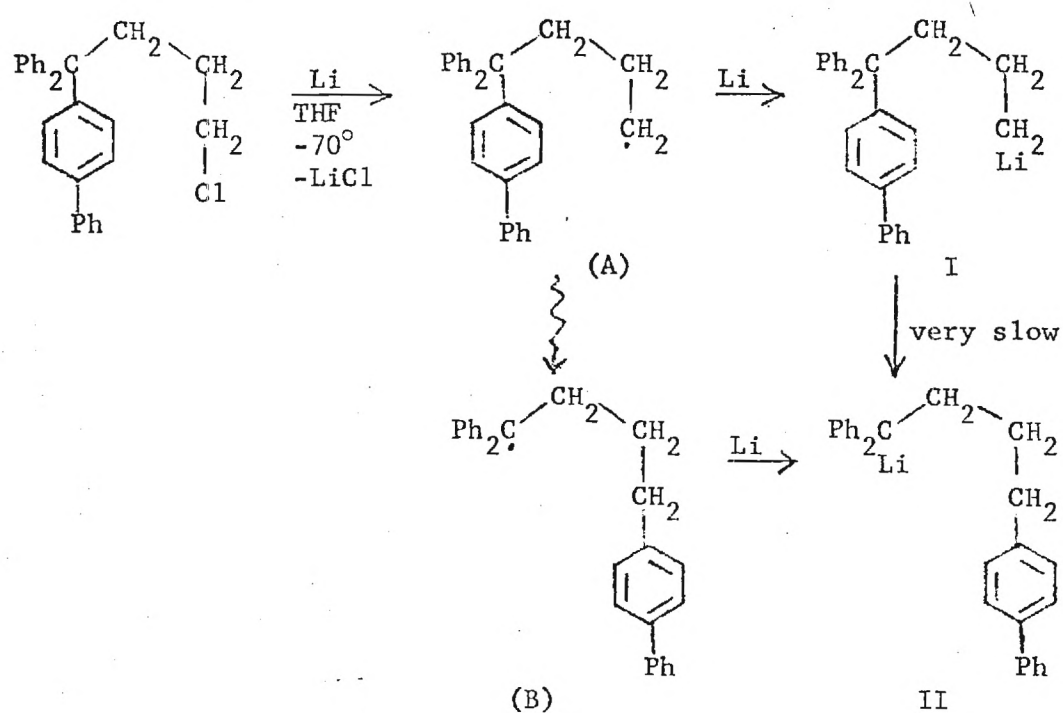
Reaction of 4-chloro-1-p-biphenyl-1,1-diphenylbutane with cesium metal in dioxane at 30 to 40° gives initially chiefly the rearranged hydrocarbon 4-p-biphenyl-1,1-diphenylbutane, which undergoes further reduction to 4-(p-cyclohexylphenyl)-1,1-diphenylbutane and the cleavage product 4-(p-cyclohexylphenyl)-1-phenylbutane.

The structures of the products of reaction of Cs-K-Na alloy in THF with diphenylmethane and 2,2-diphenylpropane have been further clarified by use of electron paramagnetic resonance. Initial experiments have been conducted upon the reaction of 1,3-diphenylpropane with Cs-K-Na alloy.

I. Organolithium Compounds Derived from 4-Chloro-1-p-biphenyl-1,1-diphenylbutane

As reported earlier,¹ lithium metal reacts with 4-chloro-1-p-biphenyl-1,1-diphenylbutane in tetrahydrofuran (THF) at -70° to give about a 75 to 25% mixture of normal (I) to rearranged organolithium product (II). We now find that when the ratio of lithium metal to chloride is increased from 15:1 to 65:1 that some 47% of the product is of rearranged structure as deduced by the products of protonation. Since the organolithium compound I rearranges to II only very slowly even at 0° , these results suggest that rearrangement occurs during preparation of the organolithium compound, presumably by way of intermediate free radicals (see Scheme I).

Scheme I



(1) E. Grovenstein, Jr., Final Technical Report upon NSF Grant No. GP-19251, pp A-6-A-7.

According to the indicated scheme the extent of rearrangement of intermediate radical (A) should depend upon how readily it is reduced to I versus how readily it rearranges to radical (B). Since in the experiments which we have just discussed, reaction takes place presumably at the surface of the lithium metal, the radicals A and B are thought to exist at or near the surface of the lithium and therefore are likely not completely "free" radicals. Such heterogeneous reactions are accordingly hard to understand in detail; in particular we do not understand why the percentage of rearrangement increases with increasing ratio of lithium to organic chloride.²

We have accordingly studied the reaction of our chloride with the homogeneous reducing agent lithium biphenyl (dissolved in THF) at -65° . Since such radical anions can transfer but one electron upon collision with an alkyl chloride, they should give rise to an intermediate free radical,³ radical (A) in our present work. Again the final outcome must be a competition between rearrangement to radical (B) versus reduction to unrearranged organolithium compound I. In the homogeneous case, however, some control over these competitive paths can be obtained by adjusting the concentration of the reducing agent lithium biphenyl. Our results for the dropwise addition of a solution of 4-chloro-1-p-biphenyl-1,1-diphenylbutane to a well stirred solution of $> 100\%$ excess lithium biphenyl in THF at -75°

(2) Various postulates might be entertained such as that rearrangement is induced by impurities in the lithium metal (Lithium Corporation of America, containing 0.05% maximum Na) or by certain (unknown) characteristics of the surface.

(3) Cf. N. L. Holy and J. D. Marcum, Angew. Chem., Int. Ed. Engl., 10, 115 (1971).

followed by decomposition with methanol are that with 0.013 M lithium biphenyl a 12:88 ratio of rearranged to unrearranged hydrocarbon [p-PhC₆H₄(CH₂)₃CHPh₂ and p-PhC₆H₄CPh₂CH₂CH₂CH₃, respectively] is produced while with 0.23 M lithium biphenyl a 2:98 ratio is obtained. It is notable, therefore, that the amount of rearrangement decreases with increasing concentration of lithium biphenyl. At the higher concentration of lithium biphenyl it is possible to prepare the organolithium product from one gram of the present chloride in absolute yields of 40 to 55% (based on the results of carbonation) with only 2 to 3% of the organolithium product being of rearranged structure. A similar technique applied to PhC(CH₃)₂CH₂Cl gave the expected organolithium compound with no more than 1.2% rearrangement (as contrasted to 5.3% rearrangement⁴ during direct reaction of this chloride with lithium metal).

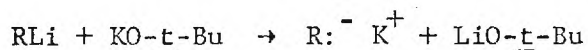
Having discovered how to make 4,4-diphenyl-4-p-biphenyllithium (I) with only a negligible amount of its rearrangement product 4-p-biphenyl-1,1-diphenylbutyllithium (II), we next turned our attention toward how to make I rearrange to II. We have already noted that I rearranges to II only very slowly even at 0° such that attempts to produce the rearrangement product by warming solutions of I result primarily in unrearranged hydrocarbon by proton abstraction from the solvent tetrahydrofuran. We have accordingly looked for a catalyst to promote this rearrangement in the cold. Since potassium t-butoxide has been found to activate

(4) E. Grovenstein, Jr., and Y.-M. Cheng, Chem. Comm., 101 (1970).

butyllithium toward metallation of hydrocarbons such as toluene⁵ and benzene,⁶ its efficacy in promoting rearrangement of our organolithium compound I has now been tested. Addition of excess potassium t-butoxide to a solution of I in THF at -75° resulted within 10 minutes in complete disappearance of I and appearance of rearranged organoalkali compound of the carbon skeleton of II as shown by products of carbonation and protonation.

We look upon this process of catalysis of the rearrangement of an organolithium compound by potassium t-butoxide (a Lewis base) as somewhat analogous to the catalysis of the Wagner rearrangement of an alkyl halide by aluminum chloride (a Lewis acid). In the former case the potassium t-butoxide gives rise to a more or less "free" carbanion, while in the latter case aluminum chloride gives a more or less "free" carbonium ion; both ions then rearrange. We believe that the demonstration of potassium t-butoxide catalysis of the rearrangement of I helps to settle the question of the mechanism of such rearrangements, i.e. it is logical that such a strong base could catalyze an anionic rearrangement, but unlikely that such a catalyst could initiate a free radical or carbonium ion process.

The details of the present catalysis merit further study. The simplest explanation is that the corresponding organopotassium compound is formed, i.e.,



(5) L. Lochmann, J. Pospisil, and D. Lim, Tetrahedron Letters, 257 (1966)

(6) M Schlosser, J. Organometal. Chem., 8, 9 (1967).

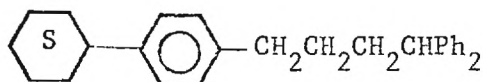
since such compounds⁷ may be precipitated from hydrocarbon solution by reaction of organolithium compounds with potassium alkoxides; however, in other cases complex aggregates⁵ of the type $\text{RLi} \cdot (\text{KO}-t\text{-Bu})_x$ or $\text{RLi} \cdot (\text{RK})_x$ may be precipitated. One peculiarity of our work on potassium *t*-butoxide catalysis is that the product, after decomposition with methanol, shows a ratio of unrearranged to rearranged hydrocarbon of about 25:75 whereas with potassium metal on the same halide in refluxing THF this ratio is 1.5:98.5 or with Cs-K-Na at -75° alloy in THF the ratio is 4:96 (after correction for Birch reduction of initial products). These results suggest that potassium *t*-butoxide catalyzes not only the rearrangement of our organolithium compound but also its protonation by solvent prior to rearrangement. Put in other words, the species undergoing rearrangement does not appear to be simply the organopotassium compound since the ratio of unrearranged to rearranged hydrocarbon is too high.

II. Reaction of 4-Chloro-1-p-biphenyl-1,1-diphenylbutane with Cesium in Dioxane

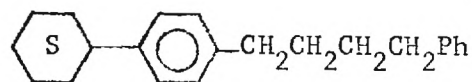
In a continuation of our studies upon the reaction of 4-chloro-1-p-biphenyl-1,1-diphenylbutane with different alkali metals in different solvents, we have now studied this halide in dioxane with cesium metal at 30 to 40° . The product with a deficiency of cesium is a 4:96 ratio of non-rearranged to rearranged hydrocarbons [*p*- $\text{PhC}_6\text{H}_4\text{CPh}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and *p*- $\text{PhC}_6\text{H}_4(\text{CH}_2)_3\text{CHPh}_2$, respectively]. The expected rearranged organocesium product was not found but only its product of protonation. Dioxane is

(7) L. Lochmann and D. Lim, J. Organometal. Chem., **28**, 153 (1971).

therefore much more acidic than tetrahydrofuran. With use of an excess of cesium metal the yield of volatile products after carbonation is greatly reduced and consisted primarily of hydrocarbons, III (15.6% yield) and IV (11.7%). Compound III is seen to be a type of Birch reduction product



III



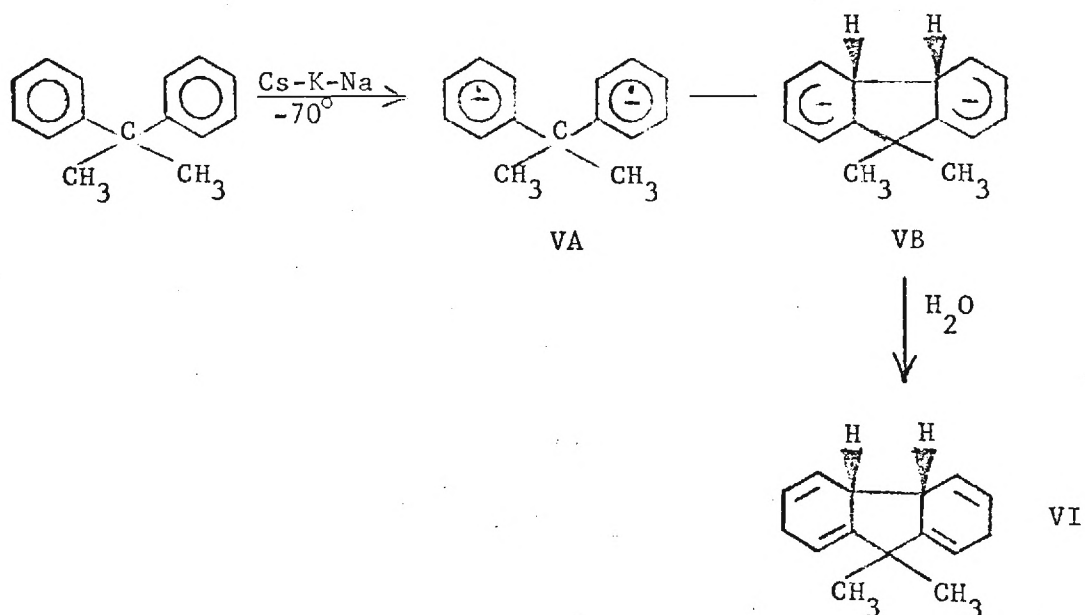
IV

while IV seems to be a cleavage product of III. Compound III is rather similar to reduction products we have obtained previously with potassium metal in THF in presence of *t*-butyl alcohol. The solvent dioxane, therefore, seems to play the same role as proton donor in these reductions as does *t*-butyl alcohol in THF.

III. Reaction of Diphenylmethane 2,2-Diphenylpropane and 1,3-Diphenylpropane with Cs-K-Na in THF

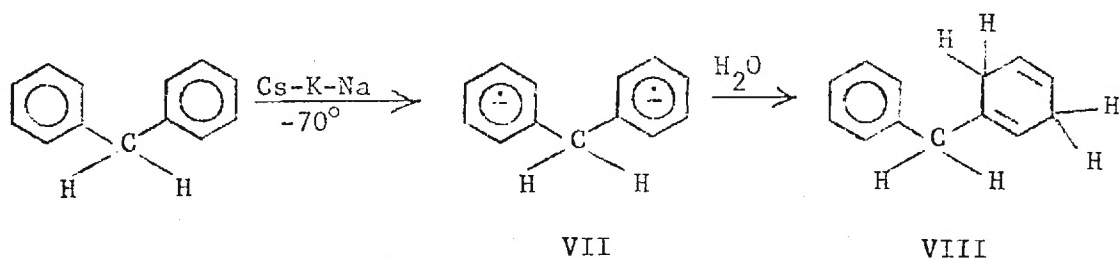
As reported earlier⁸ 2,2-diphenylpropane reacts with excess Cs-K-Na alloy in THF at -70° to give an intermediate insoluble organoalkali compound which is protonated by water to give cis-9,9-dimethyl-2,4a,4b,7-tetrahydrofluorene VI likely by the scheme:

(8) E. Grovenstein, Jr., Final Technical Report upon NSF Grant No. GP-19251, pp A-19-A-20.



In agreement with the above scheme an electron paramagnetic resonance (EPR) study of the intermediate organoalkali compound revealed negligible EPR absorption and hence the intermediate exists in a singlet state, presumably of structure VB.

In contrast similar treatment of diphenylmethane gave an intermediate organoalkali compound which gave strong EPR absorption and presumably has the diradical structure VII. Protonation of this product by water gave the Birch reduction product VIII. In our opinion the different



course of reduction of 2,2-diphenylpropane and diphenylmethane illustrates the unique character of the chemistry of insoluble ionic aggregates wherein the course of the solid state chemistry is likely to be determined by factors such as packing in crystal lattices. Under such conditions steric effects, induced in the present case by replacement of two hydrogen atoms by methyl groups, are likely to play an even more important role than in the chemistry of homogeneous solution.

1,3-Diphenylpropane has been found to react with Cs-K-Na alloy in THF and the product of this reaction is under current study by EPR and chemical techniques.

9-33-678
1 2 1 X2-7

TO: Dr. Donald A. Speer
Program Director for Chemical Dynamics
National Science Foundation
Washington, D. C. 20550

FROM: Dr. Erling Grovenstein, Jr.
Principal Investigator
School of Chemistry
Georgia Institute of Technology

SUBJECT: Annual Technical Report Upon "Chemistry of Carbanions"
NSF Grant No. GP-33367X
For Period May 1, 1972-April 30, 1973

Brief Description of Research and Results¹

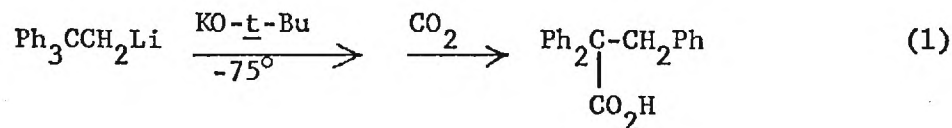
I. Rearrangements of Carbanions; Catalysis of Rearrangement of Organo-
lithium Compounds by Potassium t-Butoxide

During the present period our major research effort has been devoted to study of the rearrangement of carbanions. The most interesting and novel aspect of this work has been our discovery of catalysis of the rearrangement of organolithium compounds by potassium t-butoxide in solution in tetrahydrofuran (THF). Thus while 2,2,2-triphenylethyllithium is stable toward rearrangement in THF at temperatures of -60° or lower and indeed is only some two-thirds rearranged² to 1,1,2-triphenylethyllithium after one hour at 0° , yet upon addition of potassium t-butoxide (4 moles of KO-t-Bu per mole of total lithium compounds present), this rearrangement

(1) For further details upon this work see our "Resumé of Progress to Date upon "Chemistry of Carbanions" for period of May 1, 1972-August 31, 1972. The resumé was included in our request for a second year of support; a copy is attached.

(2) E. Grovenstein, Jr., and L. P. Williams, Jr., J. Amer. Chem. Soc., **83**, 412 (1961).

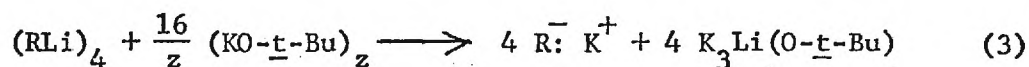
to the 1,1,2-triphenylethyl anion is complete in less than 10 minutes at -75° .



We suggest that the catalysis by potassium $\underline{\text{t}}$ -butoxide may be explained on the basis of co-association such as in eq. (2):



which in its most extreme form may be represented by eq. (3):



2,2,2-Triphenylethyllithium likely exists in THF as a tetramer as has been reported for $\underline{\text{t}}$ -butyllithium³ and $\underline{\text{n}}$ -butyllithium;⁴ co-association with potassium $\underline{\text{t}}$ -butoxide breaks up this tetrameric cluster by substituting $\underline{\text{t}}$ -butoxide anions for R^- as near neighbors for Li^+ . In the most extreme case, $\underline{\text{t}}$ -butoxide anion replaces all R^- as near neighbors of Li^+ and we may say that an organopotassium compound has been formed (eq. 3). The formation of an organopotassium compound can qualitatively account for all of the present results and is in accord with the observation that reaction of organolithium compounds with potassium alkoxides in hydrocarbon

(3) M. Weiner, G. Vogel, and R. West, Inorg. Chem., 1, 654 (1962).

(4) P. West and R. Waack, J. Amer. Chem. Soc., 89, 4395 (1967).

solution sometimes results in the precipitation of organopotassium compounds;⁵ although in other cases complex aggregates⁶ of the type $\text{RLi} \cdot (\text{KO}-\text{t-Bu})_x$ and $\text{RLi} \cdot (\text{RK})_x$ have been reported. We have previously reported² that 2-chloro-1,1,1-triphenylethane reacts with potassium at -50° in 1,2-dimethoxyethane to give the rearranged product, 1,1,2-triphenylethyl anion, a result which is in accord with the present interpretation of an organopotassium compound as the reactive species formed during potassium t-butoxide catalysis of the rearrangement of organolithium compounds.

The chief merit of the present discovery is that it permits, in a simple reliable fashion, the facile formation of an organopotassium compound (or a co-association product of comparable reactivity, see eq. 2) from a generally readily available organolithium compound at low temperature under homogeneous conditions in an ethereal solvent. Other methods of preparation are much less reproducible and effective in that they involve heterogeneous reactions (the reaction of potassium sand at -50° with 2-chloro-1,1,1-triphenylethane had to be terminated after some 20% reaction because of agglomeration of the potassium sand).^{2,7}

The discovery of potassium t-butoxide ion catalysis of the rearrangement of organolithium compounds is of theoretical interest in that

(5) L. Lochmann and D. Lim, J. Organometal. Chem., **28**, 153 (1971).

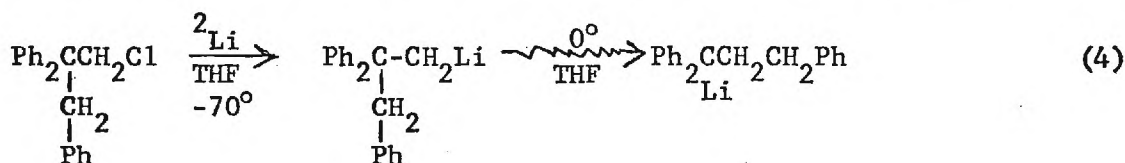
(6) L. Lochmann, J. Pospisil, and D. Lim, Tetrahedron Letters, 257 (1966).

(7) The difficulties in making organopotassium compounds by reaction of alkyl halides and dialkylmercury compounds with potassium metal in hydrocarbon media are well summarized in the work of R. A. Finnegan [Tetrahedron Letters, 1303 (1962); 429 and 851 (1963)]

this strongly basic catalyst could hardly catalyze other than an anionic reaction of an organolithium compound, much as a Lewis acid (such as aluminum chloride) catalyzes cationic reactions of alkyl halides. Other interesting aspects of potassium *t*-butoxide ion catalysis will now be discussed for individual anionic systems.

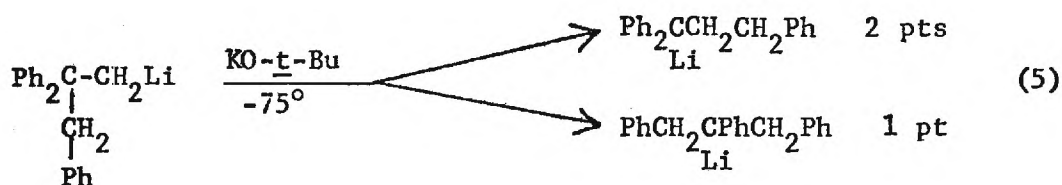
(a) Rearrangement of 2,2,3-Triphenylpropyl Alkali Metal Compounds

We⁸ have previously reported that 2,2,3-triphenylpropyllithium rearranges in THF at 0° with migration of the benzyl group (eq. 4).



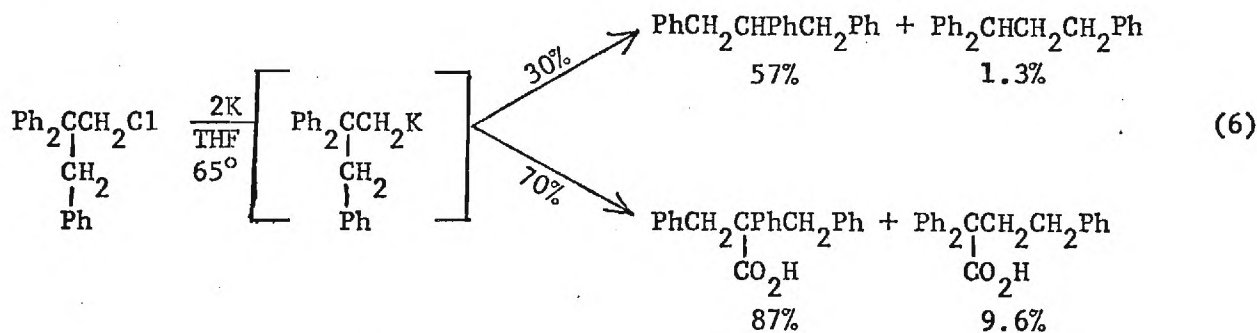
Because of other work to be reported here, this reaction has been rechecked by a careful gas chromatographic analysis of the methyl esters of the acid from carbonation and the acidic product is confirmed to consist of at least 95% of the acid of benzyl migration.

The potassium *t*-butoxide rearrangement of 2,2,3-triphenylpropyllithium has now been studied in THF at -75°. The product of carbonation was surprisingly found to consist of about a 2 to 1 mixture of the product of benzyl migration and a new product of phenyl migration (eq. 5).



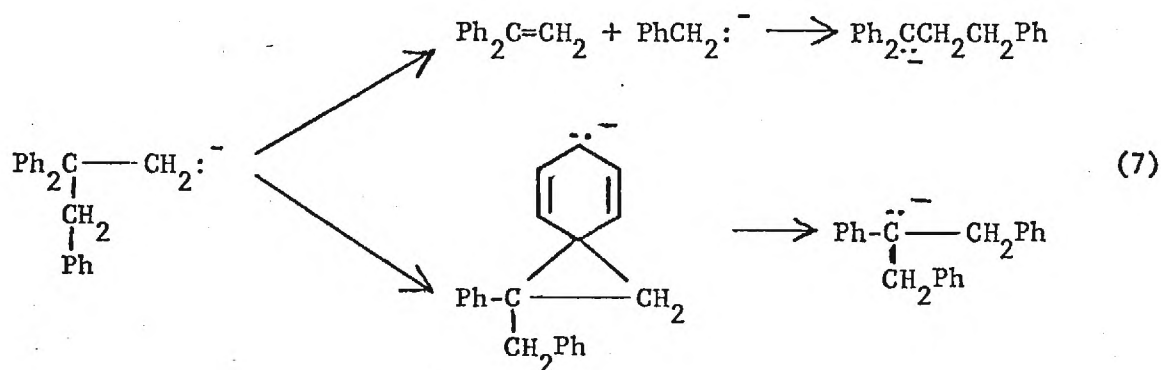
(8) E. Grovenstein, Jr., and L. P. Williams, J. Amer. Chem. Soc., **83**, 2537 (1961).

That this result does not reflect merely a temperature effect on migratory aptitudes but also a cation effect was demonstrated by study of the reaction of 1-chloro-2,2,3-triphenylpropane with molten potassium metal in THF (eq. 6).

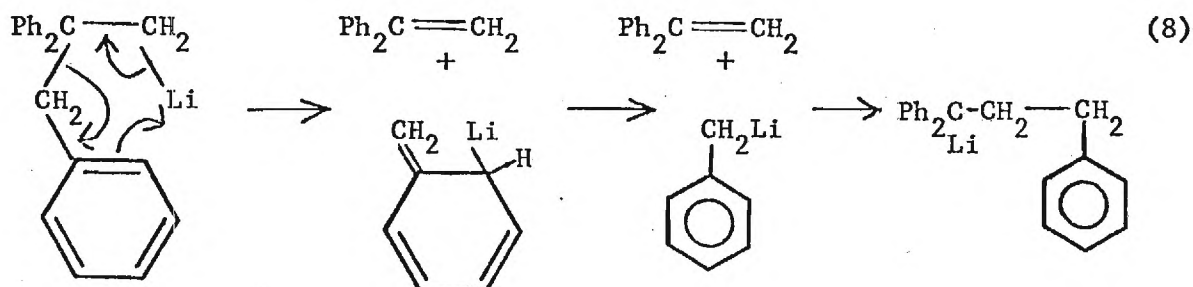


In the reaction with potassium metal the ratio of benzyl to phenyl migration was now some 1 to 11. Obviously the rearrangements catalyzed by potassium *t*-butoxide (-75°) and especially that induced by potassium metal ($+65^\circ$) have much more of the product of phenyl migration than that from the thermal rearrangement of the organolithium compound (0°). The detailed results show that the relative migratory aptitude of phenyl to benzyl increases more than 200 fold on going from lithium to potassium metal (eq. 4 vs eq. 6). Our tentative interpretation⁹ is that rearrangement of the organopotassium compound involves an ion pair in which we have a "free" or nearly "free" carbanion (for simplicity we neglect the potassium cation in our description below):

(9) For additional information on the mechanism of benzyl and phenyl migration see: E. Grovenstein, Jr., and G. Wentworth, *J. Amer. Chem. Soc.*, **89**, 1852, 2348 (1967).

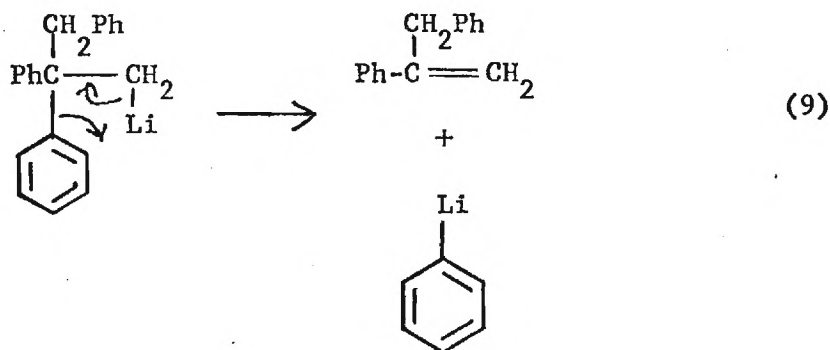


For the "free" carbanion mechanism, phenyl migration is favored over the benzyl cleavage-readdition process. In contrast, we propose that for the organolithium compound, in addition to the "free" carbanion mechanisms shown above, that a new mechanism is available which benefits from the presence of a lithium ion, at least as far as a benzyl migration is concerned. In the formation shown below (eq. 8) we neglect the degree of

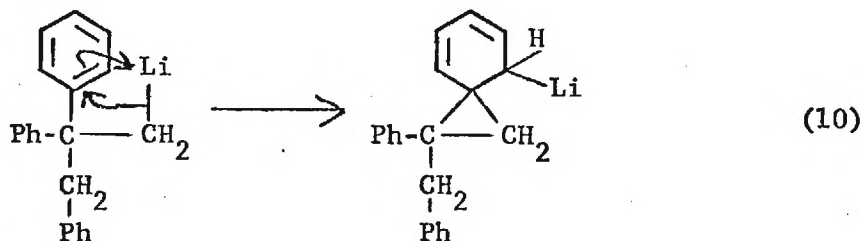


aggregation of the organolithium compound because this is unknown for the transition state; undoubtedly one coordination site on lithium must be available for the rearrangement path shown to be effected. The corresponding lithium ion promoted migration of phenyl by an elimination-readdition of phenyllithium is evidently ineffective because of the greater activation energy required for cleavage of phenyllithium vs. benzyllithium (or allylic isomer thereof); note that the cleavage of the benzyl group in

the transition state suggested for (8) involves an "aromatic" transition state of 6 electrons whereas that (9) for phenyl cleavage involves an anti-aromatic 4-electron process.¹⁰



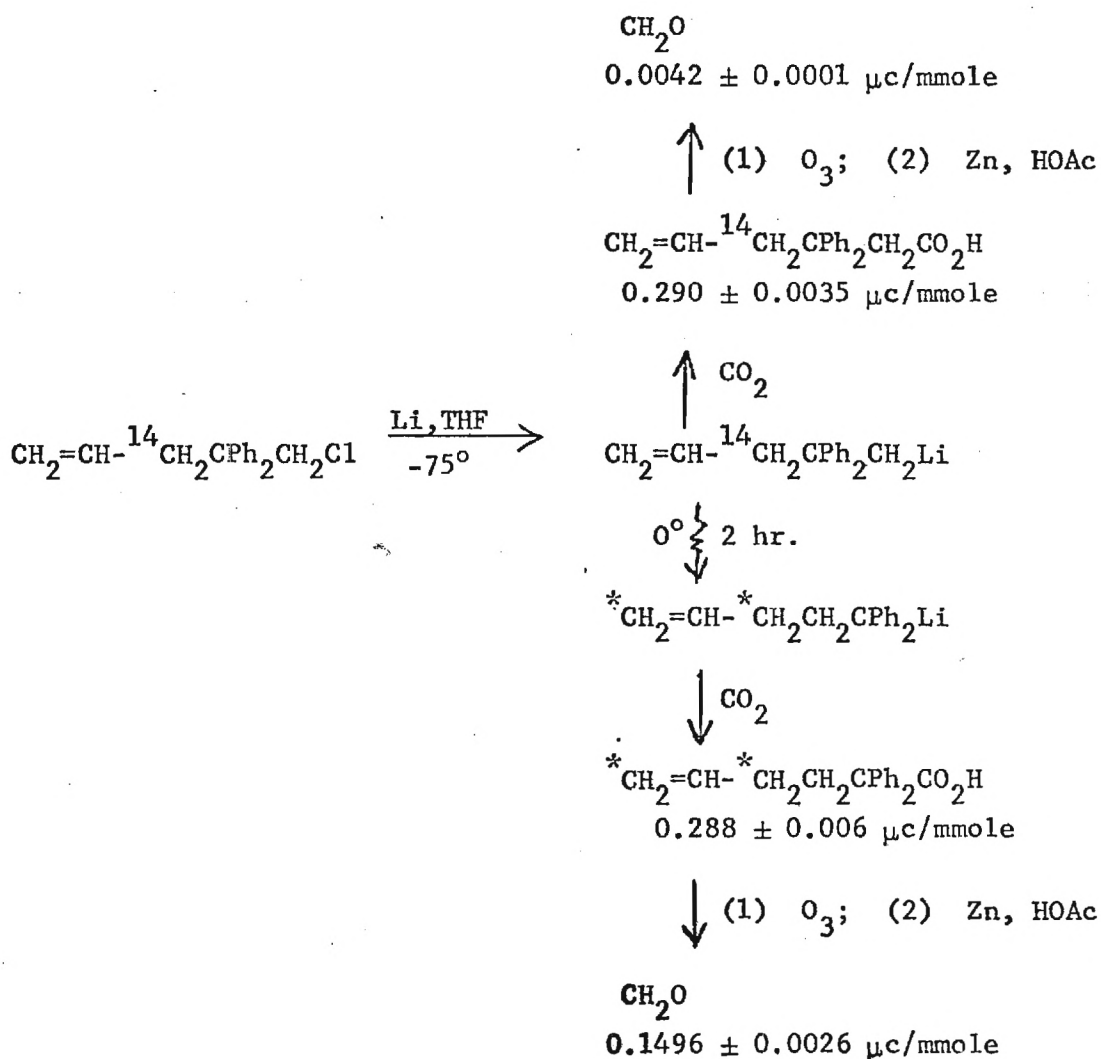
Also lithium ion catalysis of the cyclic mechanism of phenyl migration shown in (7) proceeds by way of another symmetry forbidden 4-electron process (10).



(10) Cf. P. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press., Inc., 1971, pp. 114-140. In our application of the rules of orbital symmetry to the present systems we assume that, because of its state of coördination or other reasons, lithium has but one low-lying orbital available for participation in the cyclic mechanisms depicted. This orbital is the orbital shown bonded to carbon in the reactants and products. The "forbidden" processes (eq. 9 and 10) also suffer from more steric strain in their transition states than the allowed process (eq. 8).

(b) Rearrangement of 2,2-Diphenyl-4-pentenyl Alkali Metal Compounds

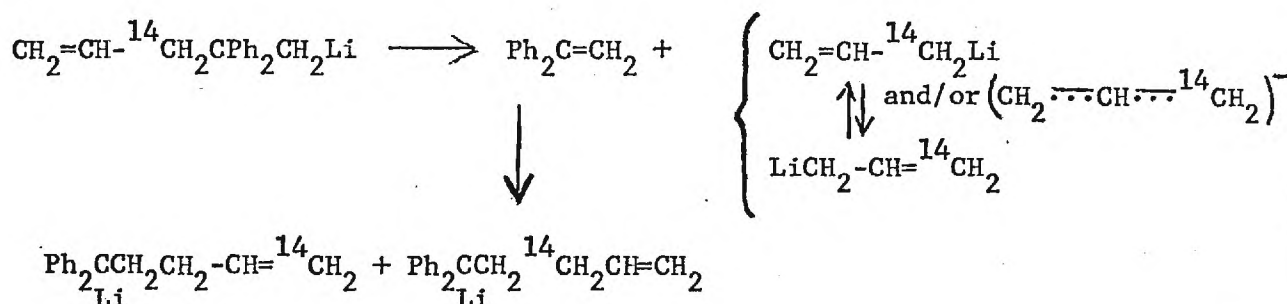
Reaction of 1-chloro-2,2-diphenyl-4-pentene-3- ^{14}C with lithium in THF gave a good yield of the expected organolithium compound which had essentially all of its radioactivity at the 3-position as shown by degradation of the product of carbonation (see Chart I).

Chart I

If, however this organolithium compound was held at 0° for two hours before carbonation, a 1,2-migration of allyl occurred and the product of carbonation

had the carbon-14 label scrambled between the two ends of the allyl group (see Chart I) as expected for a mechanism involving elimination and re-addition of allyllithium (see Chart II). The radioactivity is expected to

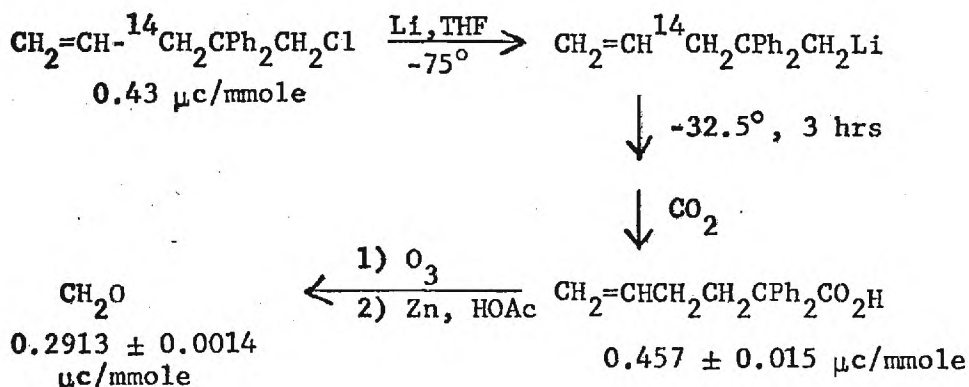
Chart II



be rapidly equilibrated between the terminal positions of the intermediate allyllithium on the basis of nmr spectral studies¹¹ upon allyllithium in ethyl ether. It is also notable in the present experiment that at least 95% of the product involved a 1,2-migration of the allyl group rather than the phenyl group.

When this experiment was repeated, except that rearrangement was allowed to proceed for 3 hours at -32.5° , the acid from allyl group migration was no longer randomly labeled at the ends of the allyl group; instead, an excess of activity resided in the terminal methylene group (see Chart III).

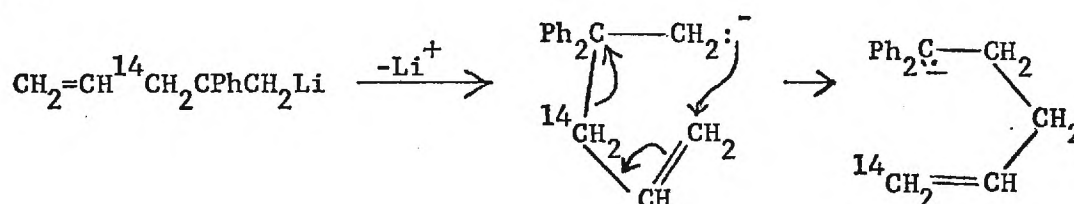
Chart III



(11) C. S. Johnson, Jr., M. A. Weiner, J. S. Vaughn, and D. Seyferth, *J. Amer. Chem. Soc.*, **83**, 1306 (1961); P. West, *et al.*, *ibid.*, **90**, 797 (1968).

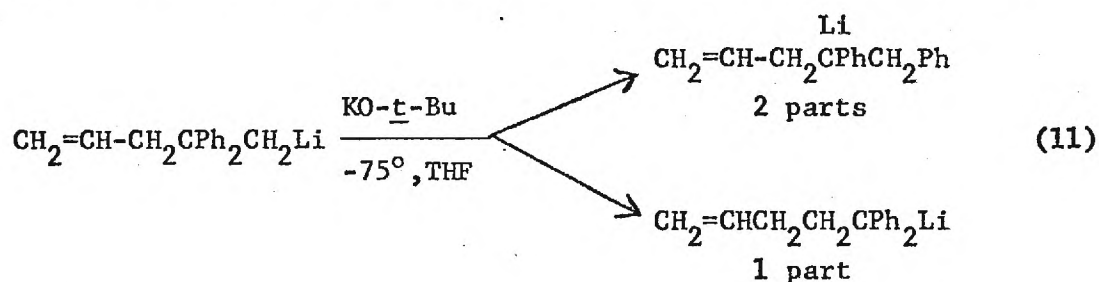
This result may be explained on the basis that some 72% of the reaction proceeded by the elimination-readdition mechanism of Chart II, while some 28% proceeded by an allylic "inversion" mechanism as shown in Chart IV.

Chart IV



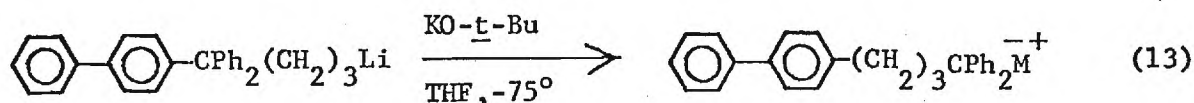
The inversion mechanism involves a concerted rearrangement via an aromatic (6 electron) transition state; this mechanism appears to be favored by low temperatures which may aid the solvation of the lithium ion.

In an attempt to obtain a predominance of the inversion mechanism, we have studied rearrangement of 2,2-diphenyl-4-pentenyllithium at -75° with catalysis by potassium *t*-butoxide. The result (see eq. 11) was that both phenyl and allyl migration occurred in about a 2:1 ratio as shown by



the products of carbonation. In contrast lithium *t*-butoxide induced no rearrangement at -75° in a time (0.5 hour) for which the rearrangement catalyzed by potassium *t*-butoxide was complete. Also the product from rearrangement in presence of lithium *t*-butoxide at 0° consisted of a 21:1 ratio of allyl to phenyl migration.

this organolithium compound brought about rearrangement (1,4-migration of *p*-biphenyl) within 10 minutes at -75° (see eq. 13). Again the results



of potassium *t*-butoxide catalysis parallel the ready migration observed in reaction of the corresponding chloride with potassium metal.

(d) Rearrangement of 4,4,4-Triphenylbutyl Alkali Metal Compounds

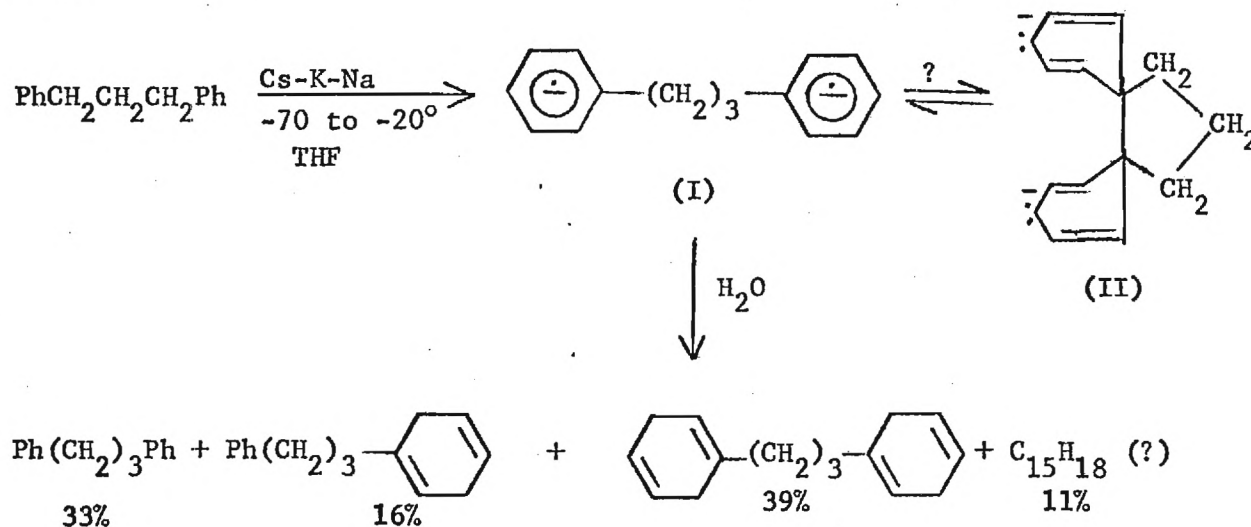
4,4,4-Triphenylbutyllithium when warmed to 25° in THF has been reported¹² to give 1,1,1-triphenylbutane but no products of rearrangement. We now find that addition of potassium *t*-butoxide to this organolithium compound followed in one minute by hydrolysis gave 9-butyl-9-phenylfluorene (41.5%), 1,1,4-triphenylbutane (4%), 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene (4.5%), and 1,1,1-triphenylbutane (50%) according to analysis by gas chromatography. Tentatively we suggest that the products come by the scheme shown in Chart V; however, the question of at what stage(s) the expected hydroaromatic compounds become fully aromatic is not yet resolved. The rearrangements observed here rival in complexity those obtained from carbonium ions. In contrast to these results the reaction¹² of 4-chloro-1,1,1-triphenylbutane with potassium metal at 65° in THF gives predominantly 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene.

(12) E. Grovenstein, Jr., J. A. Beres, Y.-M. Cheng, and J. A. Pegolotti, *J. Org. Chem.*, **37**, 1281 (1972).

II. Reactions of Aromatic Hydrocarbons with Cesium Metal and Cesium Alloys

In a continuation of our work¹ on the reaction of aromatic hydrocarbons with cesium metal and cesium alloys in THF, we now find that Cs-K-Na alloy reacts with 1,3-diphenylpropane to give what appears to be a good yield of the diradical dianion (I) (see Chart VI) as deduced from the products of quenching with ice water. While one product remains unidentified, so far no product has been found which would appear to come from the cyclic dianion (II). In future studies the question of whether the intermediate anion is a diradical or triplet molecule such as (I) or a singlet species such as required for (II) will be probed by study of the esr spectrum of the intermediate.

Chart VI



Publications

The following publications in the area of the present grant have appeared during the present grant period for work, much of which was done during prior grant periods:

- (1) "Carbanions. XI. Reactions of 4-Chloro-1,1,1-triphenylbutane, 5-Chloro-1,1,1-triphenylpentane, and 1,1,1-Triphenylethane with Alkali Metals; 1,4- and 1,5-Migration of Phenyl," E. Grovenstein, Jr., J. A. Beres, Y.-M. Cheng, and J. A. Pegolotti, J. Org. Chem., **37**, 1281-1292 (1972).
- (2) "Carbanions. XII. *p*-Biphenyl Migration in Reactions of 1-Chloro-2-*p*-biphenylethane-1,1-*d*₂ with Alkali Metals," E. Grovenstein, Jr., and Y.-M. Cheng, J. Amer. Chem. Soc., **94**, 4971-4977 (1972).
- (3) "Carbanions. XIII. 1,4-Migration of the *p*-Biphenyl Group. Formation of an Intermediate Spiro Anion," E. Grovenstein, Jr., S. Akabori, and J.-U. Rhee, J. Amer. Chem. Soc., **94**, 4734-4735 (1972).

With completion of the thesis of J.-U. Rhee (see below) the work of Rhee and Akabori appears to be ready for full publication. We are also planning a Communication to the Editor in the area of potassium *t*-butoxide catalysis.

Theses

- (1) "1,4-Migration of the *p*-Biphenyl Group in the Reactions of 4-Chloro-1-*p*-biphenyl-1,1-diphenylbutane with Alkali Metals," Ph.D. Thesis of Jung-Ung Rhee, Georgia Institute of Technology, March, 1973.
- (2) The Ph.D. thesis of Mr. Thomas Longfield (on reactions of cesium and cesium alloys with aromatic hydrocarbons) should hopefully be completed by the end of the summer, 1973, after having been delayed a year because of Mr. Longfield's acceptance of a teaching position for the past year.
- (3) The Ph.D. thesis of Mr. A. B. Cottingham (on rearrangements upon 2,2-diphenyl-4-pentenyl alkali metal compounds) should be completed near Jan. 1, 1974.

Inventions or Discoveries

Our work on potassium *t*-butoxide catalysis of the rearrangement of organolithium compounds and on variation of migratory aptitudes with choice of alkali metal may be patentable; however, the Georgia Institute of

Technology feels that the best interest of the scientific community will be served by publication of this work, rather than by filing a patent application.

Scientific Collaborators

Mr. Thomas H. Longfield - Ph.D. candidate, 4 months of support on this grant.

Mr. Auburn B. Cottingham - Ph.D. Candidate, 7 months of support on this grant.

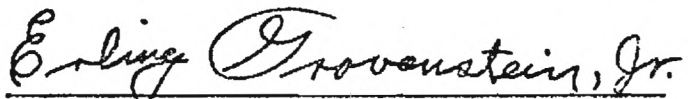
Mr. Dean E. Quest - Ph.D. candidate, 10 months of support on this grant.

Mr. Jung-Ung Rhee - Ph.D. candidate, 12 months of support on this grant.

Dr. Robert Edward Williamson - 8 months of support on this grant. Dr. Williamson is a "Teaching Post-doctoral Research Associate" and is supported half from this grant and half from funds supplied by the Georgia Institute of Technology.

Comments

This is the first year of "Continuing Research Grant" GP-33367X and an amendment of October 10, 1972, provides funds for the second year of May 1, 1973-April 30, 1974.



Erling Grovenstein, Jr.
Principal Investigator
May 15, 1973

Attachment: (1)

TO: Dr. M. Biallas
 Program Director for Chemical Dynamics
 National Science Foundation
 Washington, D. C. 20550

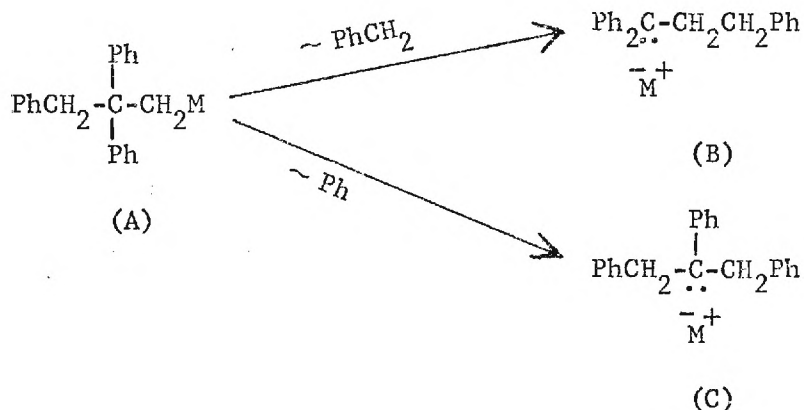
FROM: Dr. Erling Grovenstein, Jr.
 Principal Investigator
 School of Chemistry
 Georgia Institute of Technology

SUBJECT: Annual Technical Report Upon "Chemistry of Carbanions"
 NSF Grant No. GP-33367X1
 For Period May 1, 1973-April 30, 1974

Brief Description of Research and Results

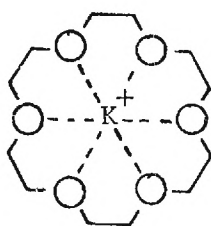
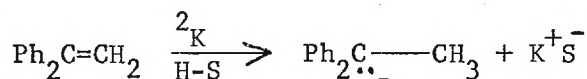
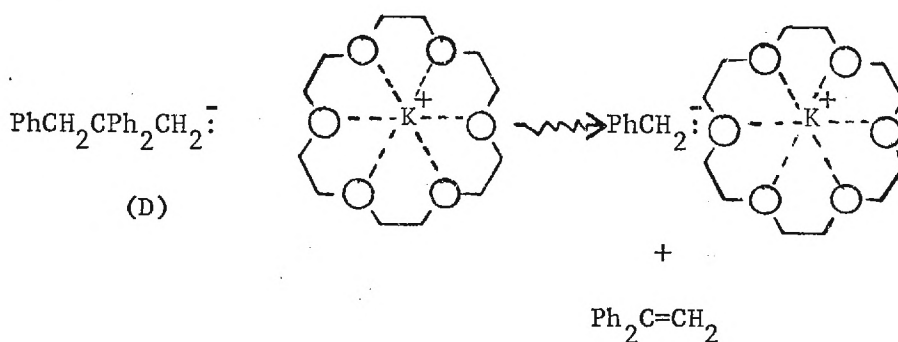
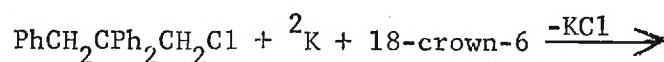
I. Rearrangements of 2,2,3-Triphenylpropyl Alkali Metal Compounds

The system 2,2,3-triphenylpropyl alkali metal compound (A) can undergo rearrangement with either 1,2 migration of benzyl to give (B) or 1,2 migration of phenyl to give (C):



During the past year considerable effort has been made to find what conditions favor migration of benzyl versus phenyl in this system. The results are summarized in Table I. It is notable that 2,2,3-triphenylpropyllithium at 0° or 2,2,3-triphenylpropyllithium plus potassium or cesium *t*-butoxide complexed with 18-crown-6 ether at -75° gives exclusively the product (B) of

benzyl migration. Also reaction of potassium with 2,2,3-triphenylpropyl chloride in THF containing 18-crown-6 ether at -75° gives the cleavage products benzylpotassium and 1,1-diphenylethylpotassium. The latter products suggest that the reaction with potassium proceeds according to the process:



(where H-S is tetrahydrofuran or 18-crown-6 ether)

This proposed mechanism is in agreement with previous observations upon 2,2,3-triphenylpropyllithium which has been suggested¹ to undergo rearrangement via an elimination readdition mechanism, in part because external

(1) E. Grovenstein, Jr., and G. Wentworth, J. Amer. Chem. Soc., **89**, 1852 (1967).

^{14}C -labeled benzyllithium becomes incorporated during the course of rearrangement:

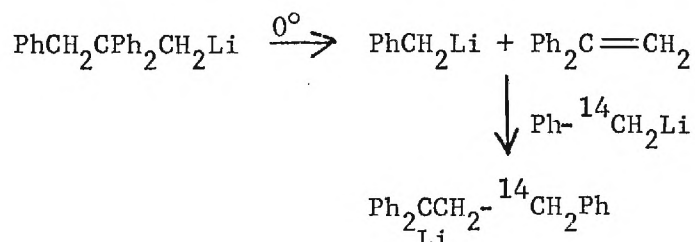


Table I. - Rearrangements of 2,2,3-Triphenylpropyl Alkali Metal Compounds in Tetrahydrofuran

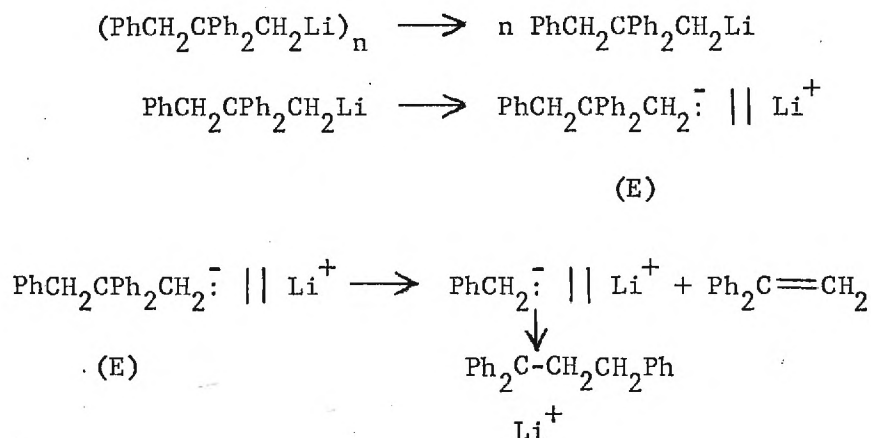
Conditions	Temp., °C	Products*, Relative Mol %		
		(B)	(C)	Other
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Li}$	0°	> 99	< 1	
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Li} + \text{KO-}t\text{-Bu} + 18\text{-crown-6}$	-75°	> 99	< 1	
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Li} + \text{CsO-}t\text{-Bu} + 18\text{-crown-6}$	-75°	> 99	< 1	
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Li} + \text{NaO-}t\text{-Bu}$	-75°	> 95	< 5	
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Li} + \text{KO-}t\text{-Bu}$	-75°	63	37	
$\text{PhCH}_2\text{CPh}_2\text{Li} + \text{CsO-}t\text{-Bu}$	-75°	21	79	
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Cl} + \text{K}$	$+65^\circ$	10 [‡]	90 [‡]	
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Cl} + \text{K} + 18\text{-crown-6}$	-75°	0.2	< 0.1	$\text{Ph}_2\text{CCH}_3(77)$, $\text{PhCH}_2\text{K}(23)$

*Yields based only on acidic products from carbonation.

‡An 8:92 ratio of (B) to (C) is obtained if the neutral hydrocarbons from carbonation are included along with the acids in the calculated ratio.

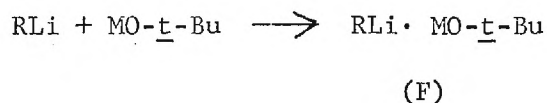
The new work with 18-crown-6 and potassium shows that the cleavage can take place readily at -75° in a crown ether separated ion pair (D). This latter observation suggests that the rearrangement of the organolithium

compound probably occurs in tetrahydrofuran (THF) in a solvent-separated ion pair (E) according to the process:



Presumably a comparatively high temperature (0°) is required to bring about rearrangement of the organolithium compound in order to induce heterolytic cleavage of the carbon-lithium bond.

The next question is why does the solvent- or crown-separated ion pair (D or E) undergo rearrangement with exclusive migration of the benzyl group rather than the phenyl group? This question is difficult to answer. The potassium *t*-butoxide catalyzed rearrangement of 2,2,3-triphenylpropyllithium (Table I) proceeds with much migration of phenyl. Still more phenyl migration is observed with cesium *t*-butoxide as catalyst. Catalysis by alkali metal alkoxide is thought to involve either a coördination complex² (F) of the organolithium reagent

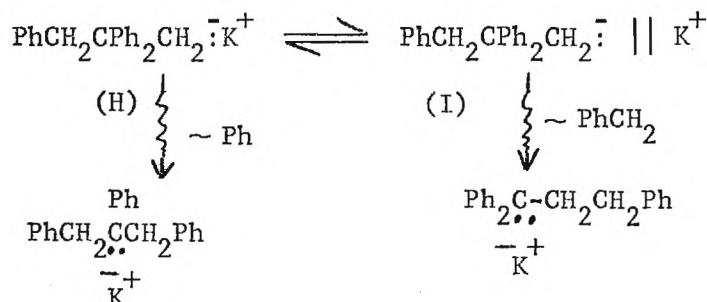


(2) M. Schlosser, *J. Organometal. Chem.*, **8**, 9 (1967);
 L. Lochmann, J. Pospisil, and D. Lim, *Tetrahedron Lett.*, 257 (1966).

or a metal exchange to give a new organoalkali compound³ (G).



If the latter interpretation is correct, potassium and cesium t-butoxide with the present organolithium reagent give rise to 2,2,3-triphenylpropylpotassium and 2,2,3-triphenylpropylcesium respectively. On this basis we attribute the 37% phenyl migration observed with potassium to rearrangement of the intimate ion pair (H) while the 63% migration of benzyl we attribute to rearrangement of the solvent-separated ion pair (I)



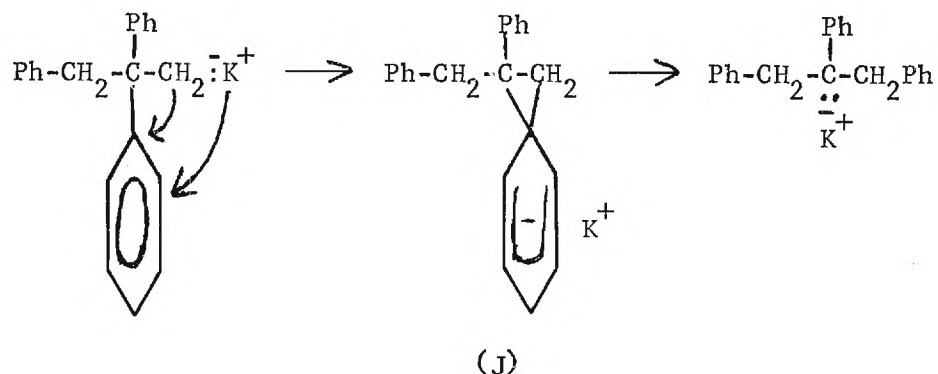
In agreement with the suggested mechanism for the potassium t-butoxide catalyzed process is the observation that cesium t-butoxide gives more phenyl migration than potassium t-butoxide. This fact is to be expected for our mechanism since 2,2,3-triphenylpropylcesium should exist⁴ more exclusively as

(3) L. Lochmann and D. Lim, *J. Organometal. Chem.*, **28**, 153 (1971); W. J. Trepka, J. A. Favre, and R. E. Sonnenfeld, *ibid.*, **55**, 221 (1973).

(4) Spectral studies show that for 9-fluorenyl anions the fraction of solvent-separated ion pairs decreases rapidly in the order: $\text{Li} > \text{Na} > \text{K} > \text{Cs}$; also the fraction of solvent-separated ion pairs increases as the temperature is lowered [T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966); see also, J. B. Grutzner, J. M. Lawlor, and L. M. Jackman, *ibid.*, **94**, 2306 (1972)].

a tight ion pair than 2,2,3-triphenylpropylpotassium. Also since more tight ion pair is to be expected⁴ at high temperature than at low temperature, the larger amount of phenyl migration observed with potassium metal at 65° than with potassium *t*-butoxide at -75° can be explained by the proposed mechanism.

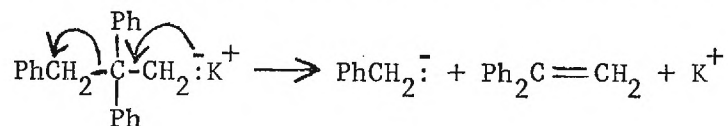
Is it logical to expect from the proposed mechanism that phenyl migration occurs largely or exclusively in a tight ion pair while benzyl migration occurs largely or exclusively in a solvent-separated ion pair? We answer this question in the affirmative. Thus for rearrangement of the intimate ion pair, phenyl may migrate in a concerted process via the spiro anion (J):



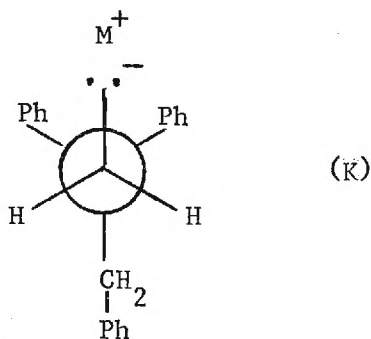
The formation of the highly reactive⁵ intermediate (J) is doubtlessly rate-determining; indeed (J) may represent the transition state for the rearrangement rather than a reactive intermediate. In the rearrangement leading to (J) the potassium cation likely accompanies the anionic center during bridging

(5) E. Grovenstein, Jr., S. Akabori, and J.-U. Rhee, *J. Amer. Chem. Soc.*, **94**, 4737 (1972); E. Grovenstein, Jr. and G. Wentworth, *ibid.*, **89**, 2348 (1967); E. Grovenstein, Jr., and L. P. Williams, *ibid.*, **83**, 2537 (1961); H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961).

such that not great separation of the charged centers is necessary for this rearrangement of the intimate or contact ion pair. In contrast for rearrangement of benzyl to occur from the ion pair the cleavage reaction shown below



gives rise to a potassium ion separated from benzyl anion by a molecule of diphenylethylene. For the cleavage mechanism it does not seem possible for the potassium ion to stay close to the anionic charge during the cleavage process; this is especially true if the elimination reaction occurs in the usual anti-periplanar conformation⁶ (K) which



is preferred especially where the leaving group is poor as in the present case. In order for the elimination of benzyl to occur from a conformation such as (H) extensive solvation is required to overcome the unfavorable separation of charge in the resulting transition state. However, conditions which are ideal for solvating the dipolar transition state are just those

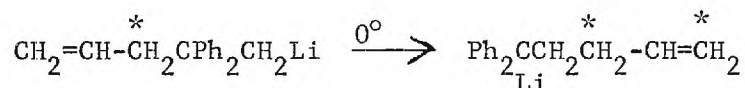
(6) See W. H. Saunders, Jr., and A. F. Cockerill, "Mechanisms of Elimination Reactions," John Wiley & Sons, New York, N. Y., 1973, Chapter III.

required for formation of solvent separated ion pairs; therefore elimination of benzyl (benzyl migration) normally occurs from a solvent-separated ion pair.

The new experimental evidence reported here has forced us to modify the tentative mechanisms which we suggested earlier⁷ for these rearrangements. An alternative, nearly equivalent, explanation of the available data is that benzyl migration occurs in a transition state which has greater charge separation than the transition state for phenyl migration. On this basis we would expect that in going from THF to a better solvating solvent such as 1,2-dimethoxyethane the percentage benzyl migration would increase while in going to a poorer solvating solvent such as diethyl ether or tetrahydropyran the percentage of phenyl migration should increase, other factors remaining constant. We hope to be able to test these postulates in the near future.

II. Rearrangements of 2,2-Diphenyl-4-pentenyl Alkali Metal Compounds

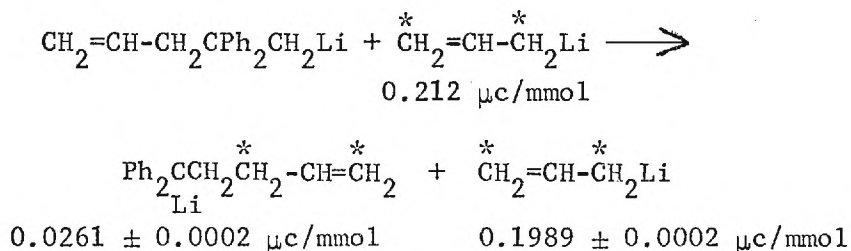
Work has continued upon study of the rearrangement of 2,2-diphenyl-4-pentenyllithium-3-¹⁴C. In our previous work⁷ it was shown that this compound rearranges in THF at 0° with essentially statistical scrambling of the carbon-14 label between the ends of the allyl group:



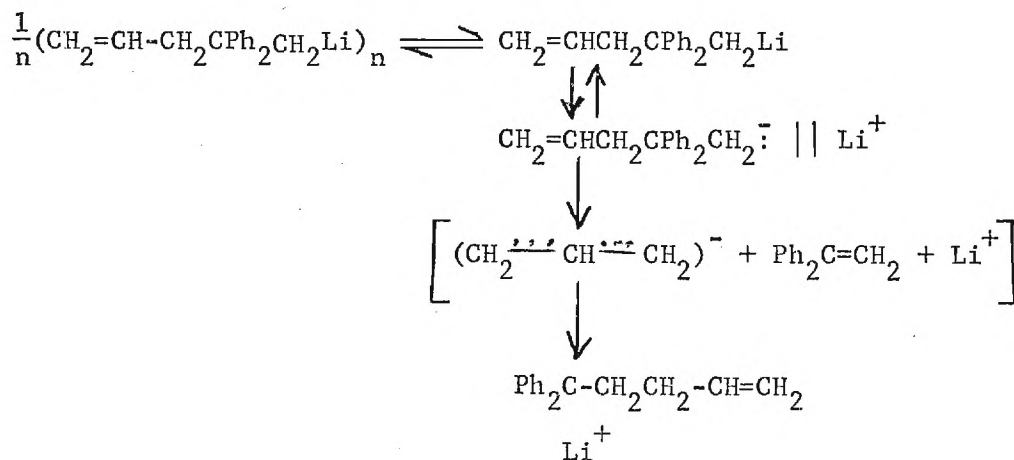
In order to determine whether or not this rearrangement is intramolecular or intermolecular the rearrangement was carried out upon non-radioactive 2,2-diphenyl-4-pentenyllithium mixed with two molar equivalents of radioactive

(7) E. Grovenstein, Jr., Annual Technical Report upon "Chemistry of Carbanions," NSF Grant No. GP-33367X, for period May 1, 1972-April 30, 1973.

allyllithium. The results are shown below:



It will be noted that the rearrangement product picked up but a small fraction of the radioactivity of the allyllithium. Had 1,1-diphenyl-4-pentenyl lithium been formed with the activity in its allyl group the same as that of the allyllithium in the surrounding solution, the activity of the final 1,1-diphenyl-4-pentenyl lithium may be calculated¹ to have been 0.167 $\mu\text{c}/\text{mmol}$. In fact the 1,1-diphenyl-4-pentenyl lithium formed had only 16% as much activity as calculated on this basis. These results may be explained by the following mechanism:



We suggest that rearrangement is promoted by an initial ionization of the organolithium compound to give a solvent-separated ion pair. The ion pair then undergoes fragmentation to form allyl anion, diphenylethylene, and lithium ion within a solvent cage. The allyl anion survives long enough to undergo several rotations such that the environment about either end of the allyl group becomes

equilibrated on a time average basis before the allyl anion adds to the diphenylethylene within the solvent. Some 16% of the allyl anions escape from the solvent cage and are replaced by allyl anions from the bulk of the solution before addition occurs.

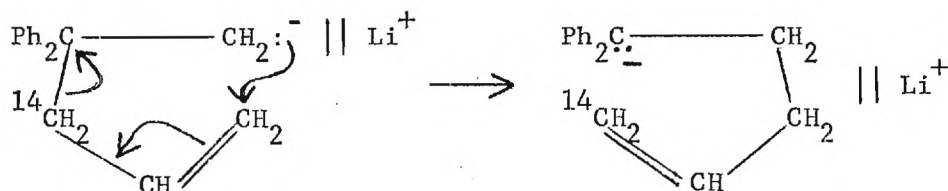
Comparison of the present results with those¹ for the rearrangement of 2,2,3-triphenylpropyllithium is interesting. For the latter case, 1,2-migration of benzyl occurred at 0° in THF with complete equilibration of the benzyllithium from the fragmentation with radioactive benzyllithium in the solution. Yet in separate kinetic studies⁸ in THF benzyllithium is reported to be 16 to 36 (dependent on the concentration) times more reactive toward addition to 1,1-diphenylethylene than allyllithium. These kinetic studies provide independent evidence that, in the present 1,2 shifts of benzyl and allyl groups in carbanions, it is not ordinary benzyllithium and allyllithium (*i.e.*, not the species predominating in THF solutions of benzyllithium and allyllithium) which are cleaved and then readded to diphenylethylene but some other species, possibly solvent-separated ion pairs. If the latter, it is not clear whether solvent-separated ion pairs of benzyllithium within the cage equilibrate more readily with benzyllithium outside the cage than solvent-separated ion pairs of allyllithium within the cage equilibrate with allyllithium outside the cage or whether solvent-separated ion pairs of benzyllithium are less reactive with diphenylethylene than similar ion pairs of allyllithium.⁹

(8) R. Waack and M. A. Doran, *J. Amer. Chem. Soc.*, **91**, 2456 (1969).

(9) An argument can be made that the first explanation is more likely to be correct on the following basis. Hückel molecular orbital calculations

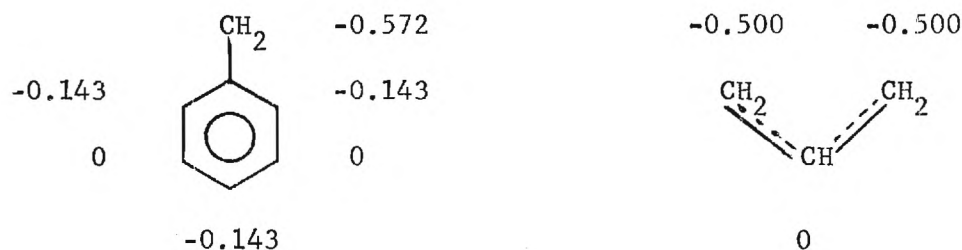
(continued on next page)

A previous experiment on rearrangement of 2,2-diphenyl-4-pentenyl-lithium-3- ^{14}C in THF at -32.5° for 3 hours indicated⁷ that 72% of the reaction proceeded by the previously given elimination-readdition mechanism whereas 28% proceeded by an alternative allylic inversion mechanism as shown below:

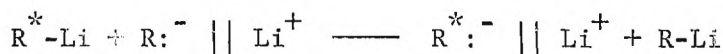


To provide better data for the new mechanism the rearrangement has been repeated at -50° for 4 days. The product after carbonation was a carboxylic

indicate that the charge distribution in benzyl and allyl anions is as follows:



Also the gain in total π -energy on localization of all of the negative charge of the benzyl anion at the α -carbon atom is calculated to be 0.720β while the gain on localization of the negative charge of the allyl anion at a single terminal carbon is 0.828β . On this basis $\text{PhCH}_2^- \parallel \text{Li}^+$ is expected to react more readily with diphenylethylene than $\text{CH}_2\cdots\text{CH}\cdots\text{CH}_2^- \parallel \text{Li}^+$, if any difference exists in their reactivity because of their unequal π -electronic structure. While benzyl anion should be a better nucleophile than allyl anion, the stronger Li-C bond in benzyllithium should retard the exchange, such that the relative rate of the exchange:

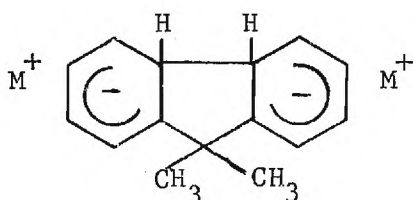


for benzyllithium versus allyllithium is difficult to predict and may depend on other factors such as diffusion rates, states of aggregation, etc.

The reactions of 2,2-diphenyl-4-pentenyllithium parallel in a remarkable way those of 2,2,3-triphenylpropyllithium likely for the reason that the allyl group is rather similar to the benzyl group. Hence we suggest that migration of allyl (either via the mechanism giving allylic inversion or that giving scrambling of the label) occurs by way of a solvent-separated ion pair while phenyl migration occurs in an intimate (contact) ion pair.

III. Reactions of Aromatic Hydrocarbons with Cesium and Cesium Alloys

In a reaction of Cs-K eutectic with 2,2-diphenylpropane in THF at about -20° , a red carbanion is formed which is believed to be largely



By carrying out the reaction with an amount of alloy containing 2.4 times the theoretical amount of cesium (assuming $M^+ = Cs^+$ in the above formula) and analyzing the alloy for the atom ratio of cesium to potassium both before and after the reaction, the following data was obtained

Cs:K, atom ratio in %

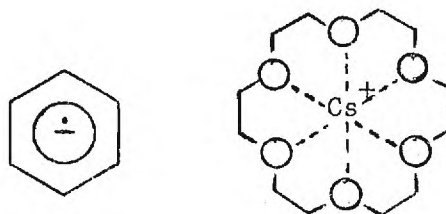
Experimental, Before Reaction: 53.6:46.4 (± 0.6)

Experimental, After Reaction: 41.1:58.9 (± 0.8)

The calculated ratio of Cs:K in the alloy remaining after reaction is 39.5:60.5 on the assumption that 100% reaction occurs to give a product of composition $Cs_2C_{15}H_{16}$. Hence the experimental results are in close agreement with those calculated. Note that in this reaction we are observing a very selective

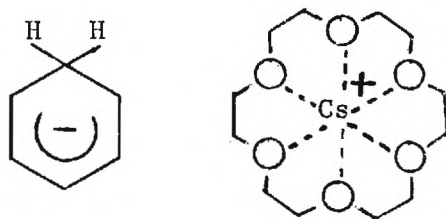
reaction of diphenylpropane with cesium in preference to potassium. We attribute this result to the smaller ionization potential of cesium and to the fact that the ionic radius¹⁰ of cesium (1.69 Å or 1.86 Å) is larger than that of potassium (1.33 Å or 1.49 Å) and about the same as the radius of a benzene ring (1.40 Å out to carbon nuclei, 2.16 Å out to the Pauling single-bond radius of carbon). Presumably cesium forms a very snug, tight ion pair with a benzenide anion or a cyclohexadienyl anion. Experiments are in progress to work upon the stoichiometry of other reactions of Cs-K and Cs-K-Na with benzenoid hydrocarbons.

In a continuation of our work⁷ on cesium benzenide, we find that addition of 18-crown-6 ether to the black precipitate of cesium benzenide from reaction of cesium sand with benzene in THF at -70° gives after warming to -5° with stirring a deep red solution which upon protonation with ice water gave an almost quantitative yield of cyclohexene and 1,4-dihydrobenzene in a molar ratio of 0.93:1.0 and only a trace of 1,1',4,4'-tetrahydrobiphenyl. These results are very different from those of protonation of ordinary black cesium benzenide (0.32:1.0 ratio of cyclohexene to 1,4-dihydrobenzene) or of its expected (at -5°) yellow-green dimerization product, which gives mainly 1,1',4,4'-tetrahydrobiphenyl. Two explanations can be advanced to explain the structure of the red anion. Possibly it is cesium benzenide complexed with 18-crown-6:



(10) M. Szwarc, "Ions and Ion Pairs in Organic Reactions," John W. Wiley & Sons, Inc., New York, N. Y., 1972, p. 3.

or alternatively it may be in part:



Experiments are in progress to distinguish between these and other possibilities.

Publications

The following paper is nearly ready for publication:

"Carbanions. XIV. 1,4 Migration of the *p*-Biphenyl Group in Reactions of 4-Chloro-1-*p*-biphenyl-1,1-diphenylbutane with Alkali Metals," E. Grovenstein, Jr., and J.-U. Rhee.

Theses

- (1) "Reactions of Cesium with Aromatic Hydrocarbons," Ph.D. Thesis of Thomas H. Longfield, Georgia Institute of Technology, November, 1973.
- (2) The Ph.D. Thesis of Mr. A. B. Cottingham (on rearrangements of 2,2-diphenyl-4-pentenyl alkali metal compounds) should be completed by the end of July, 1974.

Paper Presented

A paper entitled "Catalysis of Rearrangement of Organolithium Compounds by Potassium *t*-Butoxide," by E. Grovenstein, Jr., J.-U. Rhee, and R. E. Williamson, was presented by the senior author at the First Fall Organic Conference on "Anion Activation and Catalysis; Ion Pairs as Reactive Intermediates" on October 3, 1973, North Falmouth, Massachusetts.

Scientific Collaborators

- Mr. Auburn B. Cottingham - Ph.D. candidate, 10 months of support on this grant.
- Mr. Dean E. Quest - Ph.D. Candidate, 12 months of support on this grant.
- Mr. E. J. Jeroski - Ph.D. candidate, 3 months of support on this grant.
- Dr. Robert Edward Williamson - 12 months of support on this grant (half of his support is supplied by the Georgia Institute of Technology).

Dr. J.-U. Rhee - 2 months as research assistant after completion of his Ph.D. thesis on this project.

Comments

This is the second year of "Continuing Research Grant" GP-33367X1. An amendment of November 29, 1973 provides funds for the third year of May 1, 1974-April 30, 1975.

Erling Grovenstein, Jr.

Principal Investigator

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

CHEMISTRY

May 29, 1975

TO: Dr. Christopher J. Michejda
Associate Program Director for Chemical Dynamics
National Science Foundation
Washington, D. C. 20550

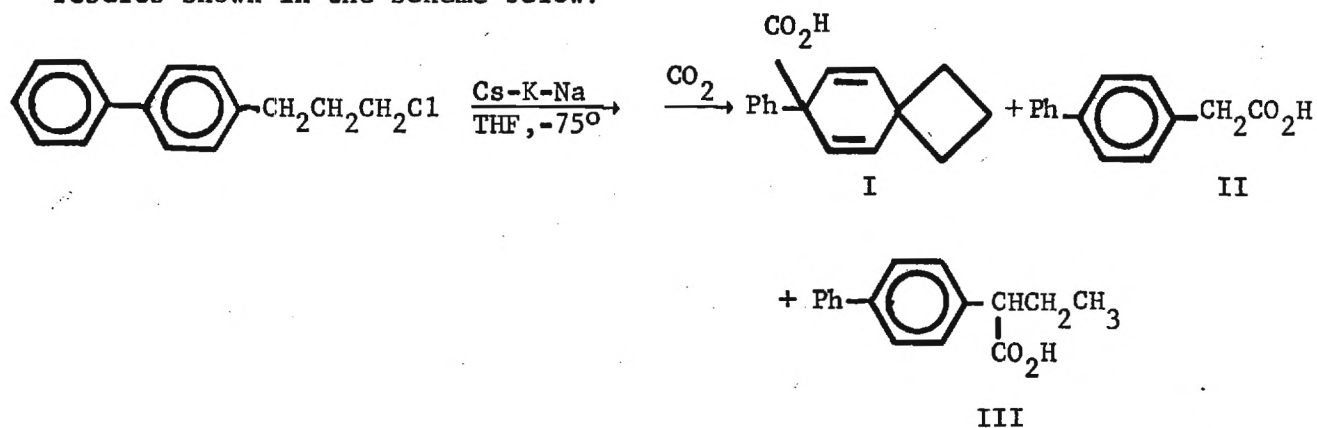
FROM: Dr. Erling Grovenstein, Jr.
Principal Investigator
School of Chemistry
Georgia Institute of Technology

SUBJECT: Annual Technical Report Upon "Chemistry of Carbanions"
NSF Grant No. GP33367X
For Period May 1, 1974-April 30, 1975

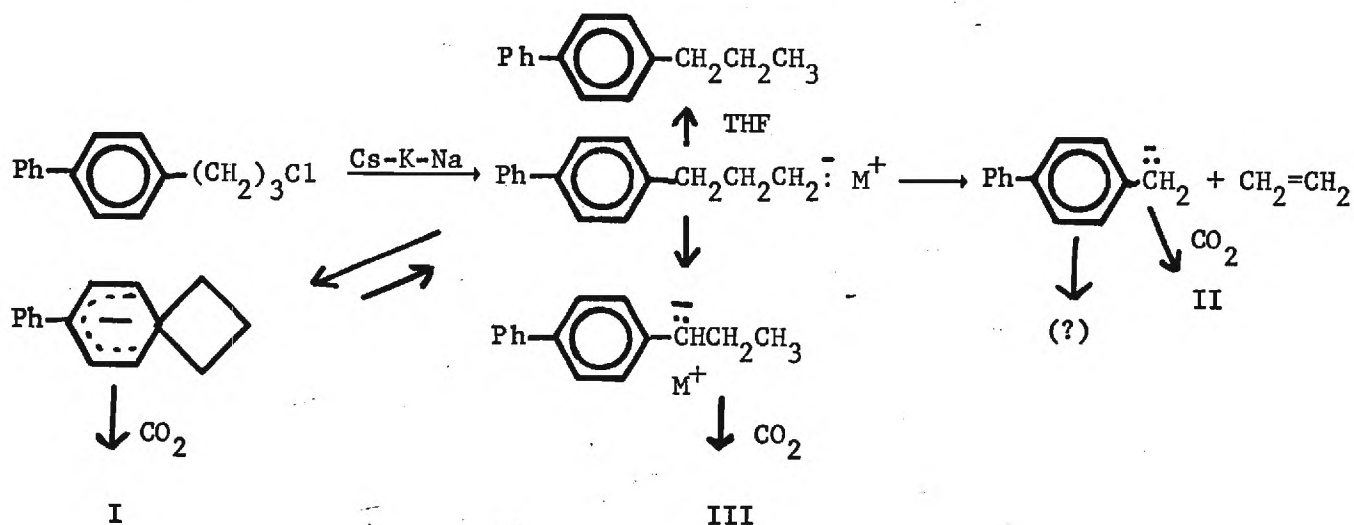
Brief Description of Research and Results

I. Rearrangements of 3-p-Biphenylpropyl Alkali Metal Compounds.

3-p-Biphenylpropyl chloride has been rapidly added to finely divided Cs-K-Na alloy in tetrahydrofuran (THF) at -75° and the product carbonated at various time intervals. Characterization of the acidic products gave the results shown in the scheme below:



These products may be accounted for by the following pathways:



In agreement with this scheme, the yield of acid I decreases with time; the intermediate spiro anion has a half-life of only some 13 minutes and disappears upon standing or raising the temperature of the reaction mixture. Acid I has been isolated in a yield as high as 36% (one minute reaction time) and thus the spiro anion is a major product of the initial reaction. The isolation of such a high yield of a derivative of the fugative spiro anion provides further evidence for spiro-cyclization as a key step in aryl migration*. Spiro anions offer interesting synthetic possibilities.

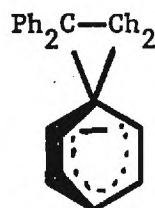
In contrast to these results, reaction of 3-p-biphenylpropyl chloride with lithium in THF at -75° gives 3-p-biphenylpropyllithium which is not appreciably rearranged even at -20° . In further work in progress in this area, 3-p-biphenylpropyllithium has been reacted with potassium *t*-butoxide (in order to prepare 3-p-biphenylpropylpotassium) and the products of the

* E. Grovenstein, Jr., S. Akabori, and J.-U. Rhee, *J. Amer. Chem. Soc.*, **94**, 4734 (1972).

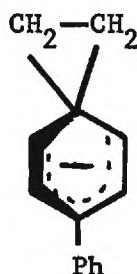
reaction studied in hopes of obtaining improved yields of I, II, and/or III. Improved yields of III are especially desirable in order to make practicable a deuterium tracer study of the detailed mechanism of formation of III.

II. Reaction of 1-Chloro-2-methyl-2-p-biphenylpropene with Alkali Metals.

While 1,2-migrations of aryl groups are believed[#] to proceed by way of cyclic transition states or intermediates such as IV from 2,2,2-triphenylethyl anion, such a spiro[2.5]octadienyl anion has so far escaped detection even in

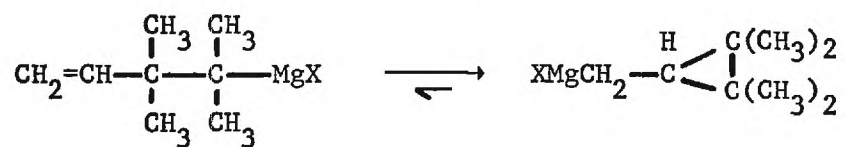


IV



V

the case of V, expected from 2-p-biphenylethyl anion which was shown (on the basis of deuterium labeling) to undergo 1,2 migration of p-biphenyl^{*}. In recent work on the rearrangement of 3-butenyl Grignard reagents, Maercker and co-workers^{##} have found that methyl groups stabilize the cyclopropylmethyl Grignard reagent much more than the open-chain form, e.g.,



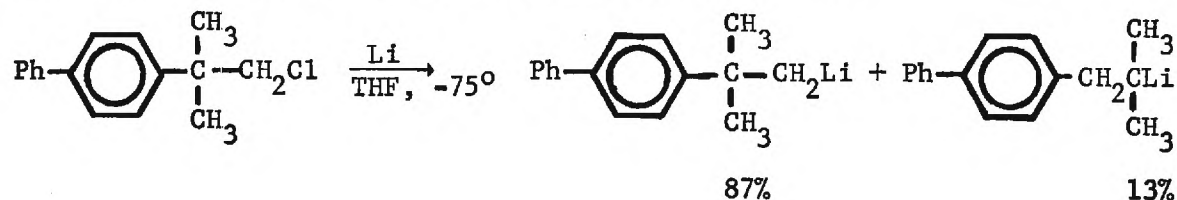
[#] E. Grovenstein, Jr., and L. P. Williams, *J. Amer. Chem. Soc.*, **83**, 2537 (1961); H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961); E. Grovenstein, Jr., and G. Wentworth, *ibid.*, **89**, 2348 (1967).

^{*} E. Grovenstein, Jr., and Y. M. Cheng, *ibid.*, **94**, 4971 (1972).

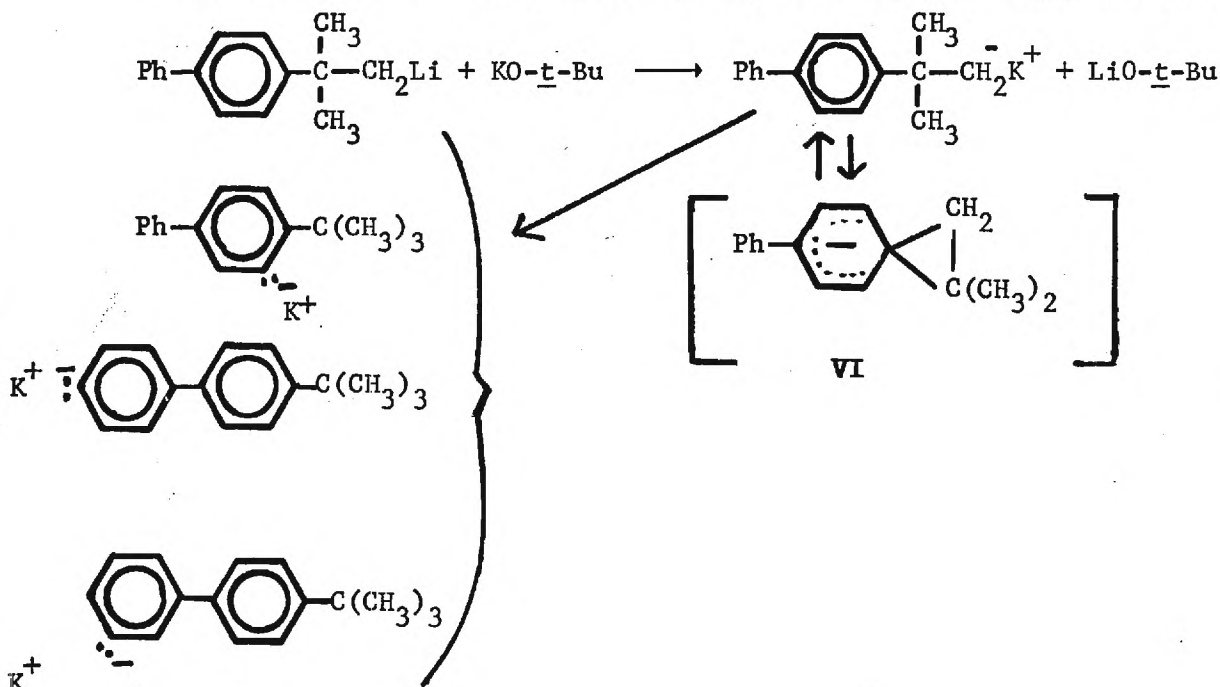
^{##} A. Maercker, P. Güthlein, and H. Wittmayr, *Angew. Chem. Internat. Edit.*, **12**, 774 (1973).

We are currently attempting to adapt this principle (Thorpe-Ingold effect) to the stabilization of V.

Reaction of lithium with 1-chloro-2-methyl-2-p-biphenylpropane in THF at -75° gives the expected 2-methyl-2-p-biphenyl-1-propyllithium along with some 13% of 2-methyl-1-p-biphenyl-2-propyllithium:



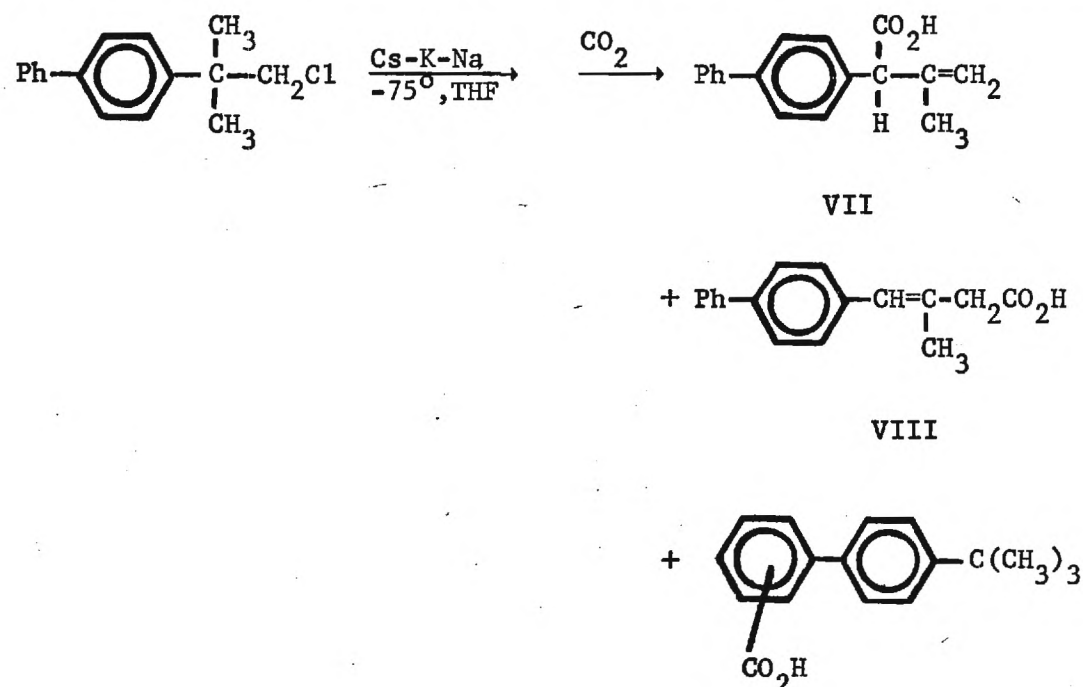
This rearrangement during reaction of the chloride with lithium metal has some precedent in the reaction of neophyl chloride with lithium*. The organolithium reagent from the above reaction was treated with excess of potassium *t*-butoxide in THF at -75° in hopes of promoting a cyclization of the resultant organopotassium compound to VI. Instead, however, they were obtained ring metallation products



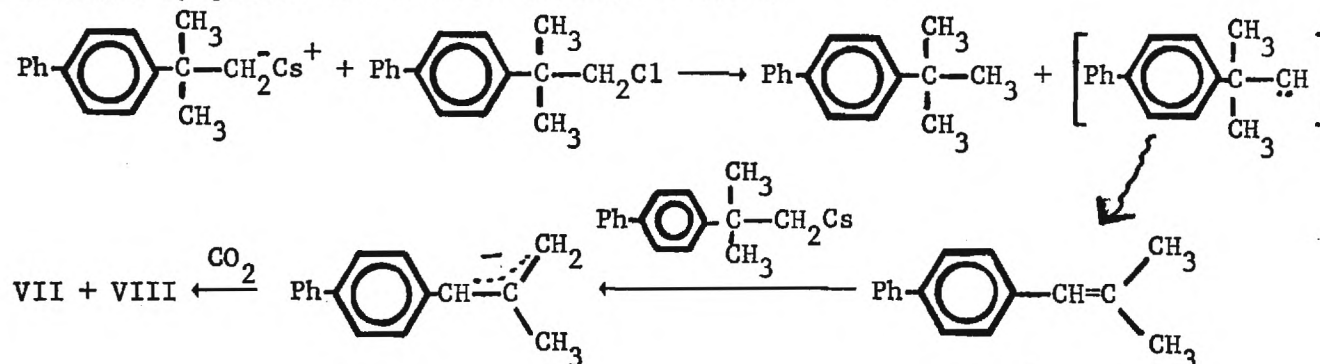
* E. Grovenstein, Jr., and Y. M. Cheng, Chem. Commun., 101 (1970).

which are tentatively identified as shown in the scheme above. This experiment demonstrates that in the time of the reaction with potassium *t*-butoxide (10 minutes), compound VI was either not formed or, if it was formed, was unstable with respect to decomposition into the observed products.

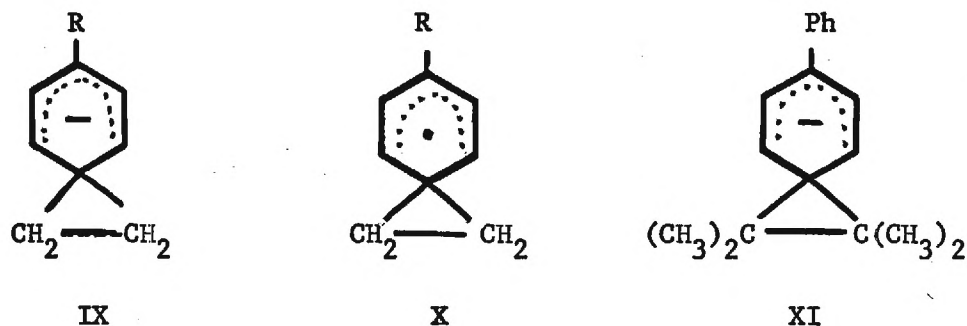
In order to carry out the above reaction on a shorter time scale, 1-chloro-2-methyl-2-*p*-biphenylylpropane was allowed to react with Cs-K-Na alloy in THF at -75° in a time as short as some 70 seconds. The products from carbonation consisted of a complex mixture of 7 carboxylic acids in which the three major more volatile products are tentatively identified as shown below:



The olefinic acids VII and VIII are believed to be formed by α -elimination followed by proton abstraction from the olefin:



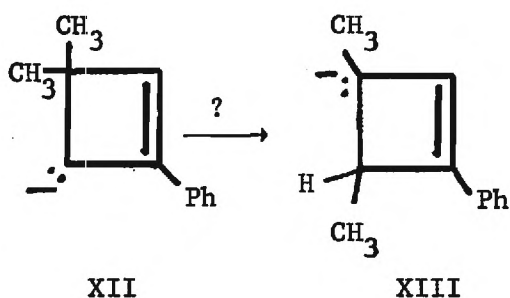
Our failure to isolate a derivative of the spiro anion VI to date provides ambiguous evidence as to whether the spiro[2.5]octadienyl anion IX is an intermediate or a transition state in 1,2 aryl migrations in anions. An analogous conclusion pertains to 1,2-aryl migrations in free radicals although the available evidence here tends to support the interpretation that the bridged structure X is but a transition state^{*}. Since an answer to the question of



whether or not structure IX exists at a potential energy minimum or a maximum would appear to be of importance to chemistry, we plan to study the more highly methylated species XI.

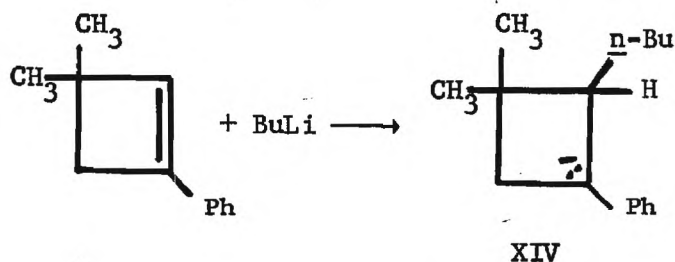
III. 4,4-Dimethyl-2-phenyl-2-cyclobutenyl Anion

The 4,4-dimethyl-2-phenyl-2-cyclobutenyl anion XII is of interest since



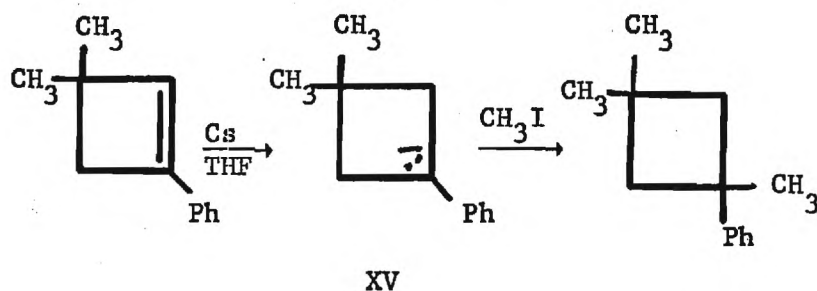
^{*} D. C. Nonhebel and J. C. Walton, "Free-radical Chemistry," Cambridge University Press, London, 1974, p. 502.

this anion offers an interesting possibility for studying the, as yet unobserved, migration of methyl in a carbanion, e.g., XII \longrightarrow XIII. Toward this end the hydrocarbon 3,3-dimethyl-1-phenylcyclobutene has been synthesized and reacted with strong bases in hopes of obtaining the desired cyclobutenyl anion XII. To date such attempts have met only with failure. Thus with n-butyl lithium in pentane activated by tetramethylethylenediamine (TMEDA) at room temperature or by potassium t-butoxide in THF at -55° or in hexane at room temperature only the product XIV of addition of n-butyl anion has been observed. Similarly t-butyllithium in pentane with TMEDA at room



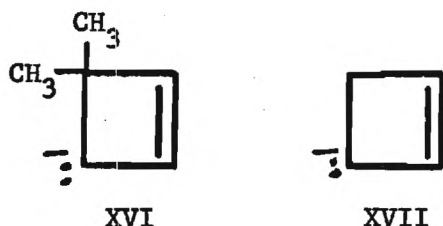
temperature gave the corresponding adduct with t-butyl anion. With the weaker base lithium diisopropylamide in THF at reflux temperature no reaction was observed nor did detectable deuterium exchange occur in presence of $\text{D-N}(\text{-i-Pr})_2$.

Also 3,3-dimethyl-1-phenylbutene was found to react with cesium metal in THF to give a red anion; however, methylation of the anion with methyl iodide gave 1,3,3-trimethyl-1-phenylcyclobutane. Thus the red anion had structure



XV rather than the desired structure XII. Reaction proceeded again to eliminate the double bond —this time by addition of electrons and protons from the solvent.

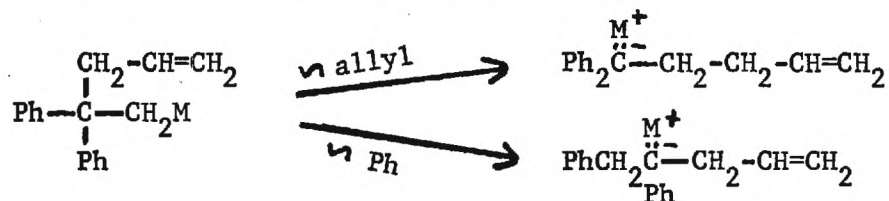
The high reactivity of the double bond in 3,3-dimethyl-1-phenylcyclobutene seems attributable to its styrene-like structure; evidently the reactivity of the double bond is also enhanced by relief of some steric strain in the adduct. What the present experiments leave unanswered is whether or not the desired anion XII may be too unstable for preparation. This might be the case if the anion is anti-homoaromatic; the related cyclobutenyl cation is thought to be homoaromatic*. Since the stability or instability of an anion such as XII is of theoretical interest, attempts to make this anion (by alternative routes) will continue. Also effort will be devoted to making the anion XVI and/or XVII without the phenyl group.



IV. 2,2-Diphenyl-4-penten-1-ylalkali Compounds

This summary includes several significant refinements of the data given in earlier progress reports. For clarity, a summary of the work from the past few years will be given.

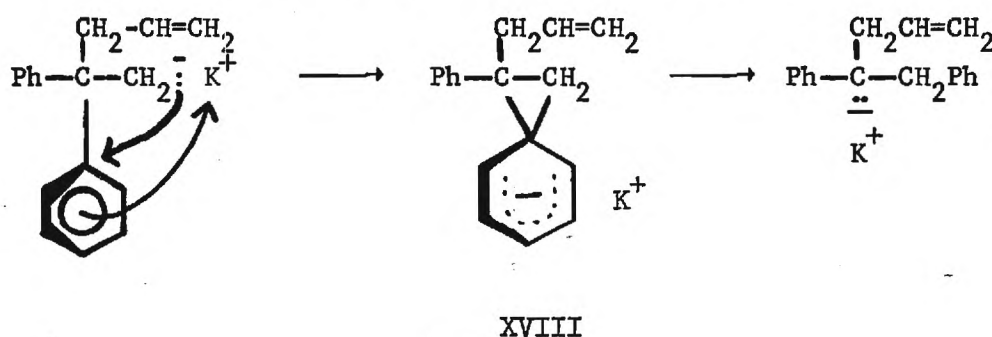
2,2-Diphenyl-4-pentenylalkali compounds have been found to undergo 1,2 rearrangement of either phenyl or allyl groups as shown below:



* G. A. Olah, J. S. Staral, and G. Liang, J. Amer. Chem. Soc., **96**, 6233 (1974).

With M being lithium in THF at -50° , 99% allyl migration and only 1% phenyl migration was observed; however, with M potassium or cesium 67% or 75% phenyl migration respectively was observed (with the remainder allyl migration) in THF at -75° . With M potassium complexed with one mole of 18-crown-6, 86% allyl and 14% phenyl migration was observed in THF at -75° . It is concluded that conditions which favor loose ion pairs (Li^+ , rather than K^+ or Cs^+ , or K^+ complexed with 18-crown-6) favor migration of allyl while conditions favoring tight ion pairs ($\text{Cs}^+ > \text{K}^+ \gg \text{Li}^+$) favor migration of phenyl.

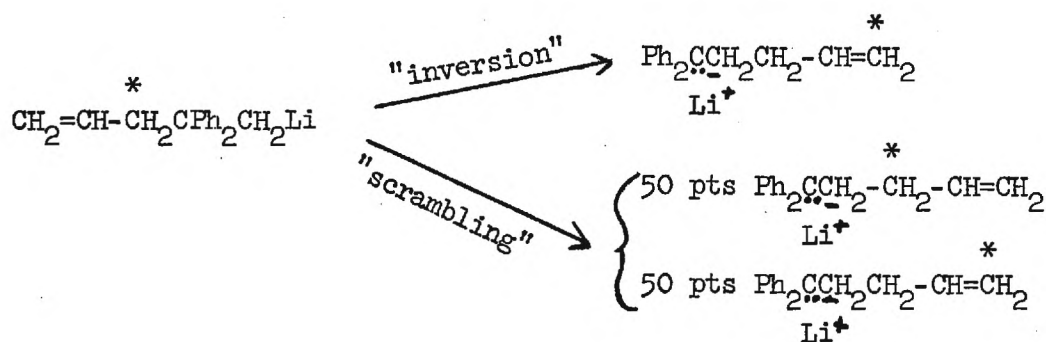
By analogy with other rearrangements^{*}, phenyl migration is believed to proceed in a tight ion pair by way of the intermediate or transition state XVIII:



In contrast, allyl migration appears to require extensive cation solvation and hence likely proceeds in a loose ion pair or a free anion.

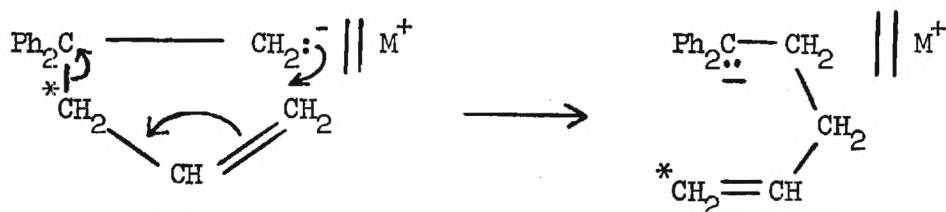
The detailed mechanism of allyl migration has been studied by use of the labeled compound 2,2-diphenyl-4-penten-1-yl- $3\text{-}^{14}\text{C}$ chloride. The reaction of this chloride with lithium metal in THF at -75° gave 2,2-diphenyl-4-penten-1-yl- $3\text{-}^{14}\text{C}$ lithium which was allowed to undergo rearrangement at 0° , -33° and -50° and gave 65%, 45%, and 33% respectively of "scrambling" with the remainder "inversion" of the allylic terminus:

^{*} E. Grovenstein, Jr., and R. E. Williamson, J. Amer. Chem. Soc., **97**, 644 (1975).



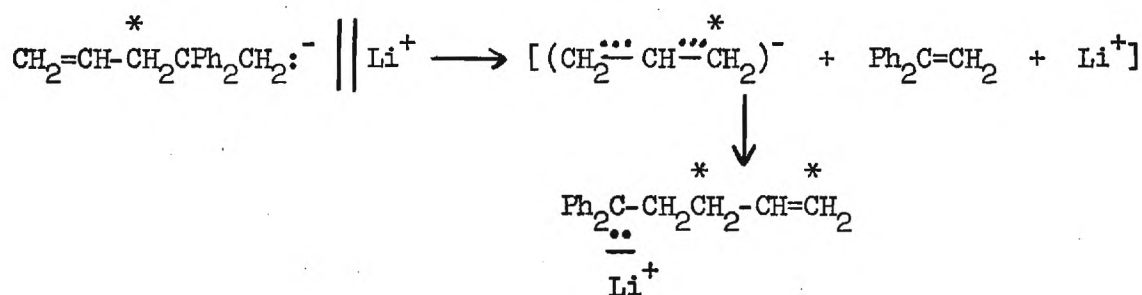
Rearrangement of the same lithium compound at -75° by the addition of five equivalents of a 1:1 complex of potassium tert-butoxide:18-crown-6 ether (which is believed to involve rearrangement of the corresponding potassium compound complexed with 18-crown-6 ether) gave an allyl migration product in which there was exclusively inversion of the allylic terminus. Addition of allyl- ^{14}C -lithium at -75° to 2,2-diphenyl-4-penten-1-yl lithium at -75° with subsequent rearrangement at 0° resulted in only 10% incorporation of ^{14}C in the product of allyl migration.

Allyl migration is believed to proceed by a duality* of mechanism. The "inversion" mechanism which preponderates at -75° is likely a concerted supra-supra [3,2] sigmatropic rearrangement in a loose ion pair (or free anion):



The "scrambling" mechanism which is favored at 0° is believed to occur in a loose ion pair (or free anion) by an elimination-readdition process:

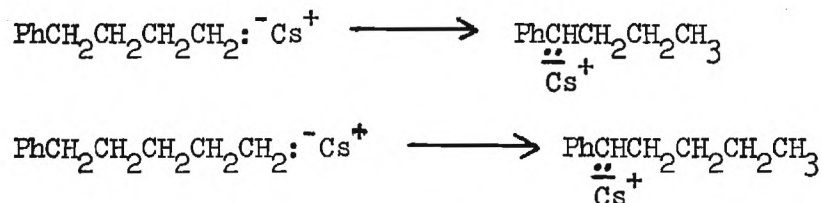
* Cf. J.E. Baldwin and F.J. Urban, Chem. Commun., 165 (1970).



In the first step allyl anion, diphenylethylene, and possibly lithium cation are formed within a solvent cage. A little of the allyl anion (ca 10%) is able to escape from the solvent cage and be replaced in the cage with external allyl anion. Presumably all of the allyl anion (at least 65% at 0°) survives in the cage long enough to undergo several rotations such that the environment about either end of the allyl group becomes equilibrated on a time average before the allyl anion adds to the diphenylethylene within the solvent cage to give the observed product. This mechanism is very similar to that which was proposed earlier for benzyl migration.*

V. Rearrangements of 4-Phenylbutyl and 5-Phenylpentyl Anions.

4-Phenylbutyl and 5-phenylpentyl anions have previously been observed (unpublished research from our laboratory) to undergo rearrangement to 1-phenylbutyl and 1-phenylpentyl anions respectively:



The work in progress is designed to elucidate the mechanism of these rearrangements.

* E. Grovenstein, Jr., and G. Wentworth, J. Amer. Chem. Soc., 85, 3305 (1963); 89, 1852 (1967).

In one experiment about an equimolar mixture of 4-phenylbutyllithium and 5-phenylpentyllithium was treated at -75° with enough potassium, t-butoxide to bring about only partial rearrangement. Carbonation of the product after 8 minutes reaction time gave 37 and 41% of rearranged carboxylic acids in the volatile acids respectively from the butyl and pentyl anions. Thus rearrangement seem to occur with about equal facility upon C_4 and C_5 side chains.

In an experiment with 4-phenylbutyllithium alone in THF at -75° , addition of excess potassium t-butoxide gave upon carbonation after 17 minutes 60% of rearranged acid (2-phenylpentanoic acid), 7.5% of un-rearranged acid (5-phenylpentanoic acid), and the remainder non-volatile acid (all yields are based upon the amount of starting organolithium reagent). This experiment suggests that a labile product is produced at some stage of the reaction and undergoes dimerization or polymerization prior to analysis. Experiments are underway to attempt to define the source of non-volatile acid. Also the preparation of deuterium labeled chlorides is nearing completion such that experiments can soon be performed to decide if the present proton migrations result from intra- or inter-molecular processes.

Publications

The following papers have been published during the past year for work supported by the National Science Foundation.

"Carbanions. XV. Tight and Loose Ion Pairs in Rearrangements of Organoalkali Compounds," E. Grovenstein, Jr., and R.E. Williamson, J. Amer. Chem. Soc., 97, 646 (1975).

"Carbanions. XIV. 1,4-Migration of the p-Biphenyl Group in Reactions of 4-Chloro-1-p-biphenyl-1,1-diphenylbutane with Alkali Metals," E. Grovenstein, Jr., and J.-V. Rhee, J. Amer. Chem. Soc., 97, 769 (1975).

"Carbanions. XVI. Reactions of 4-Chloro-1-p-biphenyl-butane with Alkali Metals," E. Grovenstein, Jr., and S. Akabori, J. Amer. Chem. Soc., 97, - - (1975). (Scheduled to appear during the summer of 1975).

Theses

The Ph.D. thesis of Auburn B. Cottingham, "The Rearrangement of 2,2-Diphenyl-4-pentenyl Alkali Metal Compounds," has now been completed and is in the hands of his Thesis Committee for approval.

Scientific Collaborators

Mr. Auburn B. Cottingham - Ph.D. Candidate, 4 months of support on this grant.

Mr. Dean E. Quest - Ph.D. candidate, 12 months of support on this grant.

Mr. E.J. Jeroski - M.S. candidate, 11 months of support on this grant.

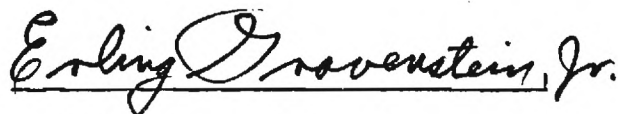
Mr. P.-C. Lu, Ph.D. candidate, 11 months of support on this grant.

Dr. Robert E. Williamson - 4 months of support on this grant (half of this support was supplied by the Georgia Institute of Technology).

Dr. Leslie T. Gelbaum - 9 months of support on this grant (half of this support was supplied by the Georgia Institute of Technology).

Comments

This is the third year of "Continuing Research Grant" GP-33367X. An amendment of Nov. 4, 1974, provides funds for a fourth year which should end about Dec. 31, 1975, at the current rate of spending of funds.



Erling Grovenstein, Jr.
Principal Investigator

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ATLANTA, GEORGIA 30332

CHEMISTRY

April 30, 1976

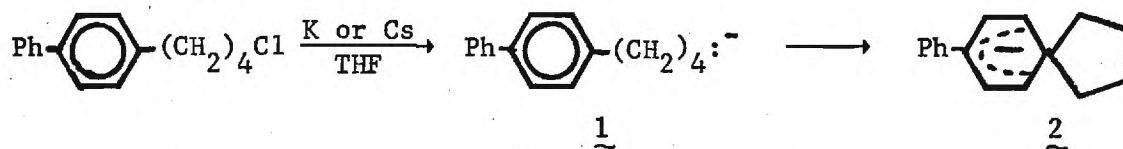
TO: Dr. Christopher J. Michejda
Associate Director for Chemical Dynamics
National Science Foundation
Washington, D. C. 20550

FROM: Dr. Erling Grovenstein, Jr.
Principal Investigator
School of Chemistry
Georgia Institute of Technology

SUBJECT: Final Technical Report upon "Chemistry of Carbanions"
NSF Grant No. MPS 72-04579 A03 (Formerly GP33367X)
For Period: May 1, 1972-April 30, 1976

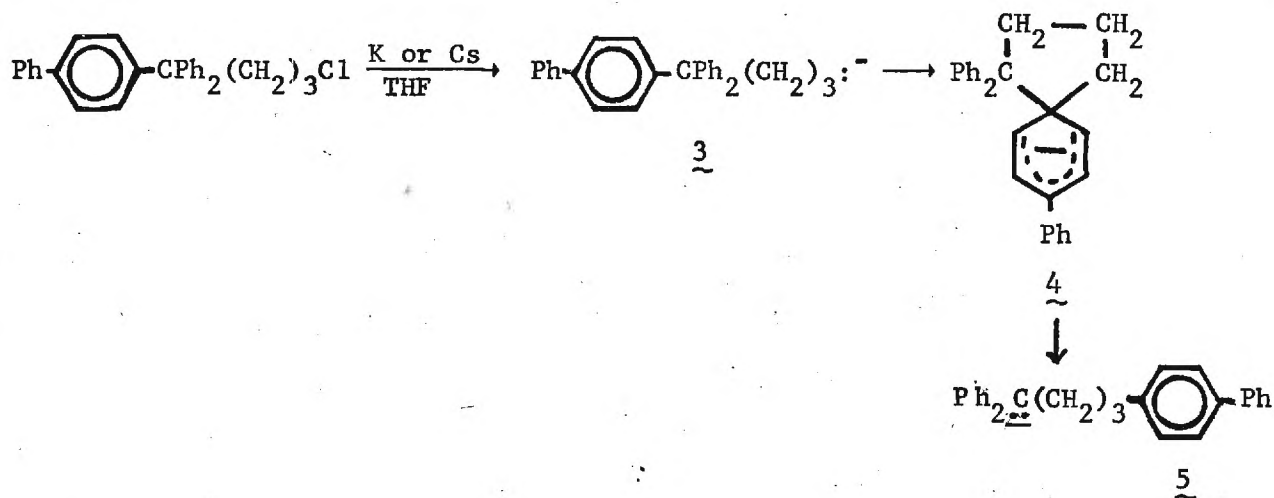
Brief Description of Research and Results*

While spiro anions have long been suggested as intermediates or transition states in 1,2-migrations of aryl groups in arylalkyl anions, such anions prior to the present work had never been directly observed or detected. Early in the present grant period we³ reported that reaction of 4-chloro-1-p-biphenylbutane with Cs or K gave 4-p-biphenylbutyl anion 1 which rapidly cyclized to the spiro anion 2 which is reasonably stable in tetrahydrofuran



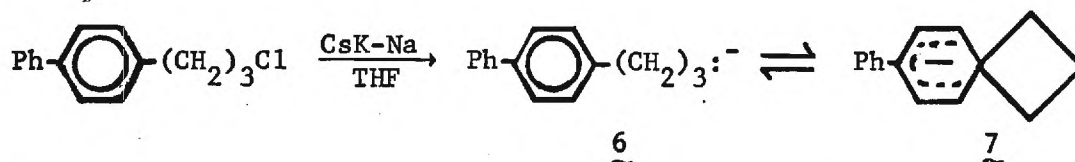
at room temperature. The discovery of spiro anion 2 confirms that the 1,4-migration of p-biphenyl observed¹ during reaction of 4-chloro-1-p-biphenyl-1,1-diphenylbutane with Cs and K occurs via the spiro anion 4,

* For further details upon this work see our "Résumé of Progress to Date upon "Chemistry of Carbanions" for period May 1, 1972-July 31, 1975. This résumé was included in our grant renewal application; a copy is enclosed.

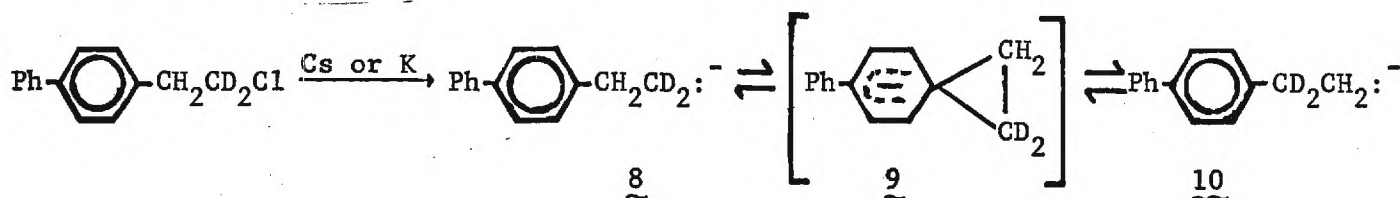


although attempts to observe 4 even at -75° were unsuccessful because of the facile rearrangement of 4 to 5. The initial formation of the arylbutyl anions 1 and 3 during these reactions was confirmed by trapping of 1 and 3 by protonation with weak acids (such as alcohols) prior to cyclization.

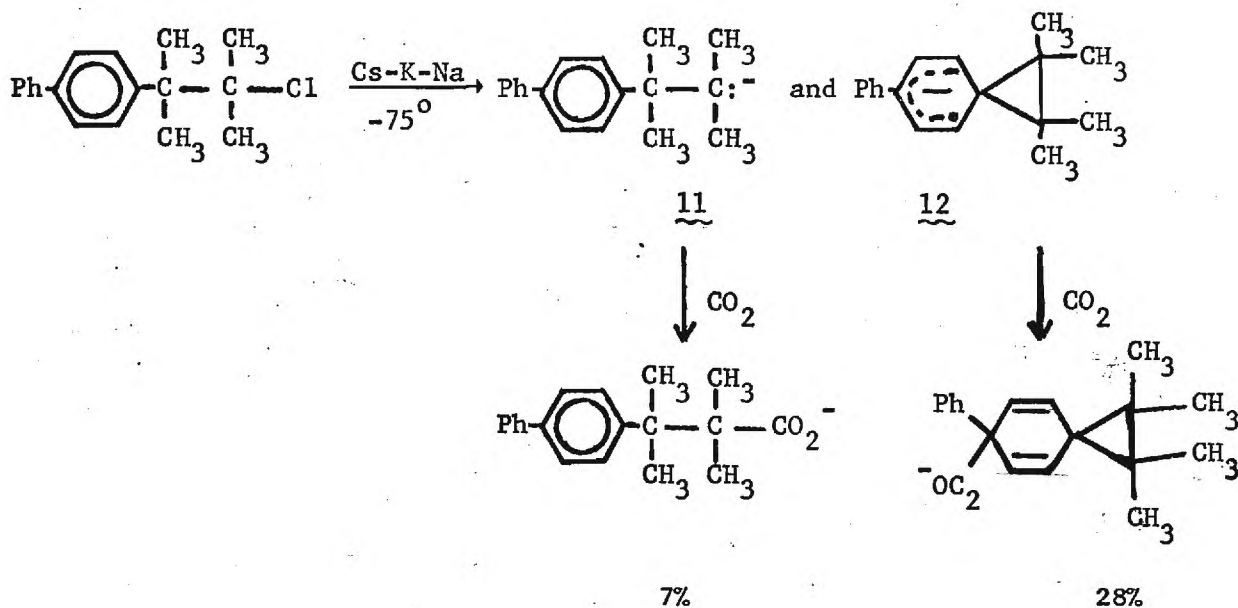
The successful observation of spiro anion 2 encouraged us to look for intermediate spiro anions in other systems. We found during the present work that the spiro anion 7 is formed in reaction of 3-*p*-biphenylpropyl chloride with Cs-K-Na alloy in THF at -75° but that this anion has a half-life of only some 13 minutes and disappears upon standing or raising the temperature of the reaction mixture.



While rearrangement of *p*-biphenyl is observed during reaction of 2-1-*p*-biphenylethyl chloride with Cs and K, we have so far been unable to detect the suspected intermediate 9. However in very recent work we find



that 3-p-biphenyl-2-chloro-2,3-dimethylbutane reacts with Cs-K-Na alloy in THF at -75° to give the spiro anion 11 and the open anion 12 as confirmed by the acids isolated on carbonation in the yields stated after a reaction time



of one minute. Further work showed that the spiro anion 12 has a half-life of some 22 minutes at -75° . In future work it is hoped to demonstrate whether or not 11 is a precursor of 12 and if 11 and 12 exist in reversible equilibrium. The evident greater stability of spiro anion 12 compared to spiro anion 9 reflects the stabilizing effect of methyl groups on small rings (Thorpe-Ingold effect).

Our success in preparing the spiro anions 7 and 12 was made possible by our development of the technique of reacting organic compounds with the liquid ternary alloy of cesium, potassium, and sodium at Dry Ice temperatures. In further work on reaction of Cs-K-Na alloy with alkyl halides and aromatic hydrocarbons, we have established that it is primarily the metal cesium in the alloy which is the reactive component (in tetrahydrofuran).

For rearrangement of 2,2,3-triphenylpropyllithium in tetrahydrofuran we have discovered² that under one set of conditions essentially exclusive 1,2-benzyl migration occurs, under other conditions 1,2-phenyl migration is observed, and under yet other conditions a mixture of phenyl and benzyl migration occurs. The factors which control the migratory aptitude of groups in this system

have been explored in some detail and a theory proposed to explain the results. This study makes an important contribution toward understanding and controlling the rearrangements of carbanions and has proven useful in a study⁴ of the rearrangement of allyl versus phenyl in 2,2-diphenyl-4-pentenyl alkali metal compounds. In the latter system a dual mechanism for migration of allyl has been demonstrated by use of carbon-14 as label for one end of the allyl system.

Publications

1. "Carbanions. XIV. 1,4 Migration of the *p*-Biphenyl Group in Reactions of 4-Chloro-1-*p*-biphenyl-1,1-diphenylbutane with Alkali Metals," E. Grovenstein, Jr., and J.-U. Rhee, J. Amer. Chem. Soc., **97**, 769 (1975).
2. "Carbanions. XV. Tight and Loose Ion Pairs in Rearrangements of Organoalkali Compounds," E. Grovenstein, Jr., and R. E. Williamson, J. Amer. Chem. Soc., **97**, 646 (1975).
3. "Carbanions. XVI. Reactions of 4-Chloro-1-*p*-biphenylbutane with Alkali Metals. Formation of a Spiro Anion," E. Grovenstein, Jr. and S. Akabori, J. Amer. Chem. Soc., **97**, 4620 (1975).
4. "Carbanions. XVII. Rearrangements of 2,2-Diphenyl-4-pentenyl Alkali Metal Compounds," E. Grovenstein, Jr., and A. B. Cottingham, manuscript in preparation.

Additional publications are planned to cover the other research described in this progress report; in most cases, however, additional experiments need to be performed to complete the work.

Theses

1. "Reactions of Cesium with Aromatic Hydrocarbons," Ph.D. Thesis of Thomas H. Longfield, November, 1973.
2. "1,4 Migration of the *p*-Biphenyl Group in the reactions of 4-Chloro-1-*p*-biphenyl-1,1-Diphenylbutane with Alkali Metals," Ph.D. Thesis of Jung-Ung Rhee, March, 1973.
3. "The Rearrangement of 2,2-Diphenyl-4-pentenyl Alkali Metal Compounds," Ph.D. Thesis of Auburn B. Cottingham, September, 1975.
4. The M. S. Thesis of Mr. Edward J. Jeroski (on [1,4] and [1,5] migration of protons in ω -phenylalkyl anions) should be completed by the end of the spring, 1976.
5. The Ph.D. Thesis of Mr. Dean E. Quest (on reactions of cesium and cesium alloys with aromatic hydrocarbons and alkyl chlorides) should be completed by the end of the summer, 1976.

Inventions or Discoveries

Much of our research effort has been devoted to extending knowledge of carbanion (and free radical) rearrangements. While this research is of both theoretical and practical importance, it is not in general of the type for which patents are sought. The best interests of the public and of the scientific community, in the opinion of the Principal Investigator, will be served by publication of the work rather than by filing patent applications.

Scientific Collaborators

Mr. A. B. Cottingham - Ph.D. candidate, 21 months support on this grant.
Dr. Leslie T. Gelbaum - post-doctoral associate, 20 months of support (half-time pay) from this grant; the remainder of his support was from Georgia Tech (for teaching a maximum of 12 hrs/week during academic year, no teaching during summer).
Mr. Edward J. Jeroski - M.S. candidate, 22 months of support from this grant.
Mr. Thomas H. Longfield - Ph.D. candidate, 4 months of support from this grant.
Mr. Pang-Chia Lu - Ph.D. candidate, 19 months of support from this grant.
Mr. Dean E. Quest - Ph.D. candidate, 42 months of support from this grant.
Mr. Jung-Ung Rhee - Ph.D. candidate, 14 months of support from this grant.
Dr. R. Edward Williamson - post-doctoral associate, 24 months of support (half-time pay) from this grant; the remainder of his support was from Georgia Tech (for teaching a maximum of 12 hrs/week during academic year, no teaching during summer).

Comments

This investigation is being continued under NSF Grant No. CHE76-02720.



Erling Grovenstein, Jr.
Principal Investigator
April 30, 1976

EG/mw

Résumé of Progress to Date upon "Chemistry of Carbanions"

For Period May 1, 1972-July 31, 1975

NSF Grant No. GP-33367X

by Erling Grovenstein, Jr., Principal Investigator

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Resumé of Progress to Date upon "Chemistry of Carbanions"

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NSF Grant No. GP-33367X

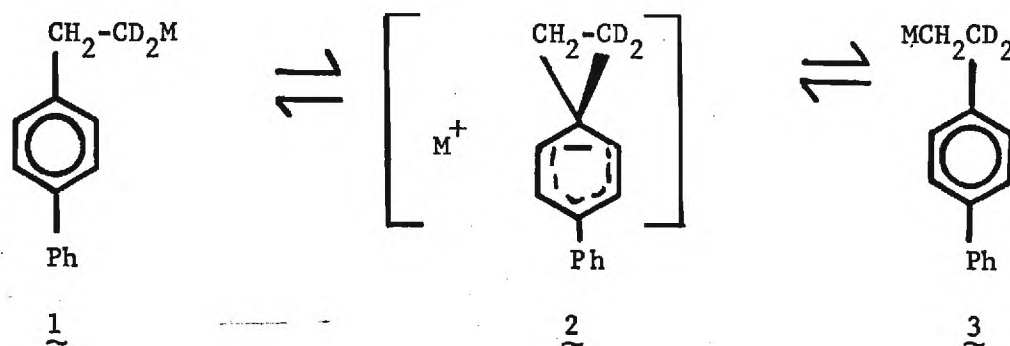
by Erling Grovenstein, Jr., Principal Investigator

PART I. Studies upon Rearrangements of Carbanions

The simplest reaction which a carbanion (i.e., an organoalkali metal compound) can undergo would appear to be a molecular rearrangement. Since knowledge about the occurrence or non-occurrence of such a reaction would appear necessary for successful procedures using carbanions as synthetic reagents and because carbanions are the most useful of the three possible trivalent forms of carbon in organic syntheses, especially for formation of new carbon-carbon bonds, most of our efforts have been directed toward learning the structural features and reaction conditions necessary for rearrangements of carbanions.

A. [1,2] Rearrangement of p-Biphenyl in 2-p-Biphenylethyl Anions

Our study of the rearrangement of the 2-p-biphenylethyl anion has now been published¹. While 2-p-biphenylethylpotassium and -cesium underwent ready

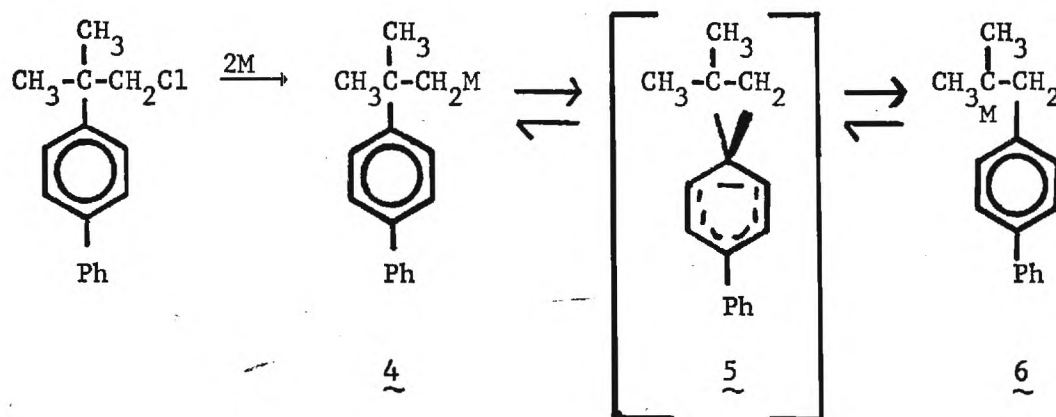


rearrangement (1 \rightarrow 3) in tetrahydrofuran (THF), the corresponding organolithium compound did not undergo appreciable rearrangement in THF at 0° even in presence

(1) E. Grovenstein, Jr., and Y.-M. Cheng, J. Amer. Chem. Soc., **94**, 4971 (1972).

of four molar equivalents of N,N,N',N'-tetramethylethylenediamine. The questions remaining unanswered from this work are: Is structure 2 an intermediate or a transition state? Under what conditions, if any, does the organolithium compound 1 undergo rearrangement to 3?

In an attempt to resolve the former question, the reaction of 2-p-biphenyl-2-methylpropyl chloride with alkali metals has been studied. The strategy here was an effort to stabilize the spiro anion 2 by methyl substitution ("Thorpe-Ingold effect"²) as in 5. From a reaction of the chloride with Cs-K-Na alloy in THF at -75°, only complex products were isolated (chiefly products from α -elimination of HCl from the chloride followed by rearrangement to 1-p-biphenyl-2-methylpropene and metallation of the olefin) and no product directly derived from the spiro anion 5 was obtained. In a reaction of the chloride

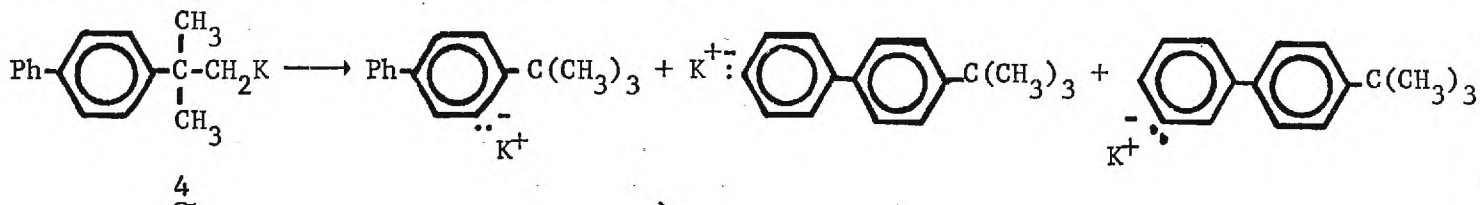


with lithium metal at -75°, the product from carbonation corresponded to 87% of 4 and 13% of 6 (M = Li) with none of 5 in evidence. The rearrangement observed during reaction of 2-p-biphenyl-2-methylpropyl chloride with lithium is thought to occur in an intermediate free radical rather than by way of the organolithium compound 4 by analogy with the corresponding reaction of 2-methyl-2-phenylpropyl chloride with lithium³.

(2) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc. New York, 1962, pp 197-202; A. Maercker, P. Güthlein, and H. Wittmayr, Angew. Chem. internat. Edit., 12, 774 (1973).

(3) E. Grovenstein, Jr., and Y. M. Cheng, Chem. Commun., 101 (1970).

Finally, in an attempt to generate a reactive 4 ($M = K$) without the complications of α -elimination the organolithium compound 4 ($M = Li$) was treated with excess of potassium *t*-butoxide in THF at -75° . There were obtained ring metallation products which are tentatively identified as shown below:

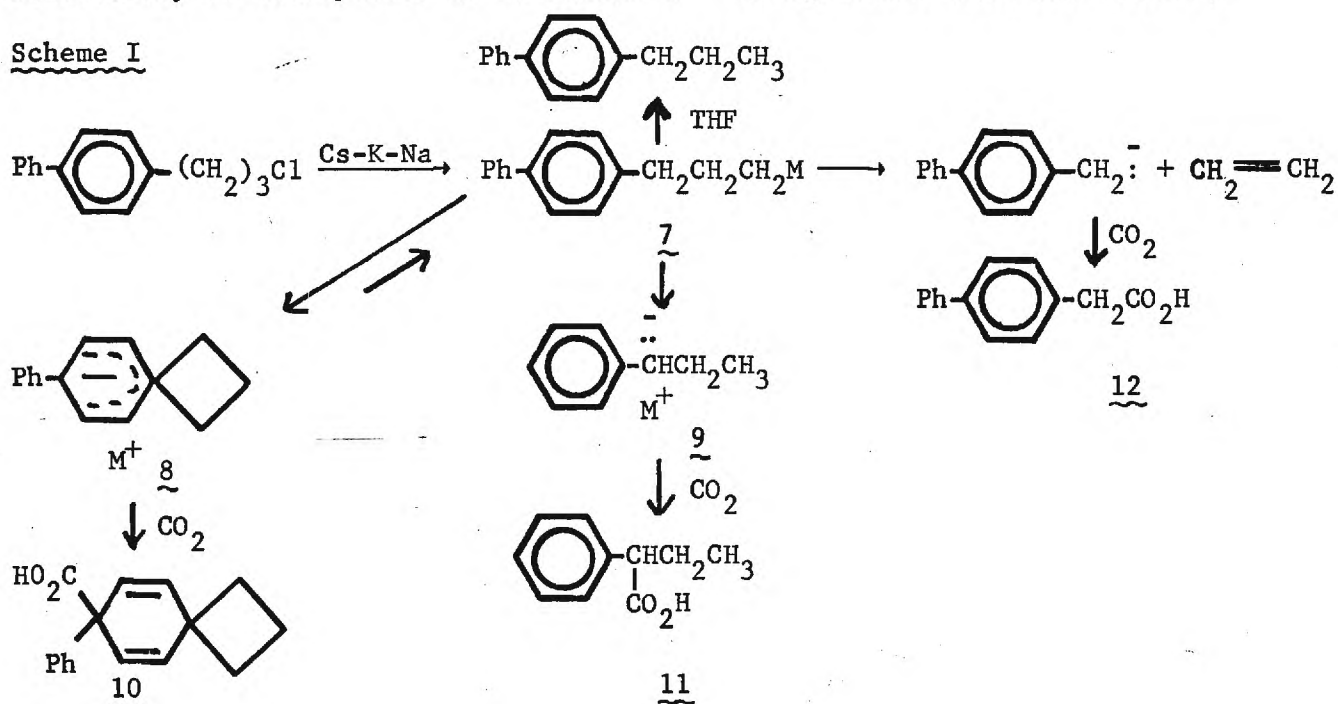


Evidently compounds 5 and 6 are less stable than the ring metallation products and hence two methyl groups in 5 do not provide adequate stabilization for detection of 5 by ordinary chemical means even though some of the conditions used were successful for the higher homolog 8 (see next section).

B. [1,3] Rearrangement of *p*-Biphenyl in 3-*p*-Biphenylpropyl Anion.

3-*p*-Biphenylpropyl chloride has been rapidly added to finely divided Cs-K-Na alloy in THF at -75° and the product carbonated at various time intervals. The results may be interpreted as in Scheme I. In agreement with this scheme,

Scheme I

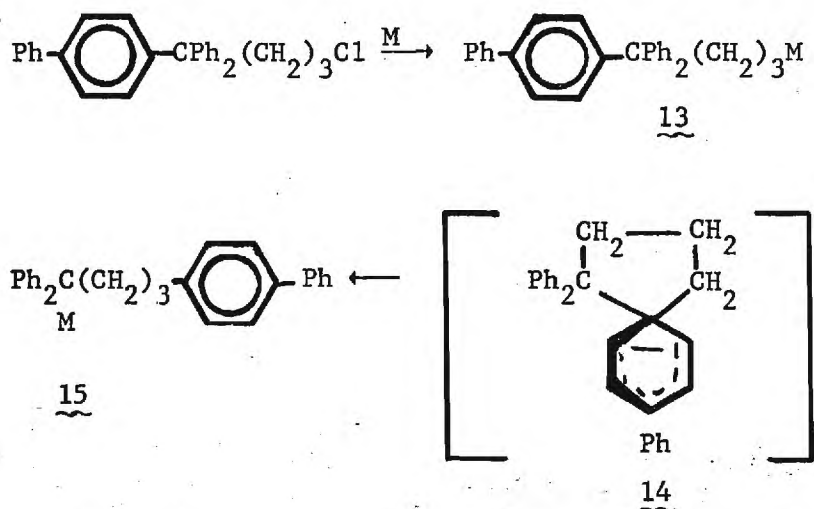


the yield of acid 10 decreases with time; the intermediate spiro anion 8 has a half-life of only some 13 minutes and disappears upon standing or raising the temperature of the reaction mixture. Acid 10 has been isolated in a yield as high as 36% (one minute reaction time) and thus the spiro anion is a major product of the initial reaction. The isolation of such a high yield of a derivative of the fugative spiro anion provides direct evidence for spiro-cyclization as a key step in aryl migration. Spiro anions offer interesting synthetic possibilities. In contrast to these results with Cs-K-Na alloy, reaction of 3-*p*-biphenylpropyl chloride with lithium in THF at -75° gives 3-*p*-biphenylpropyllithium (7, $M = Li$) which is not appreciably rearranged even at -20° . Treatment of 3-*p*-biphenylpropyllithium in THF with cesium *t*-butoxide at -75° evidently gives 3-*p*-biphenylpropylcesium since about the same mixture of products is obtained as shown in Scheme I for direct reaction of the chloride with Cs-K-Na alloy.

C. [1,4] Rearrangement of *p*-Biphenyl in 4-*p*-Biphenylbutyl Anions.

Our work on [1,4] rearrangement of the *p*-biphenyl group has been published⁴⁻⁶; hence only the high lights of this work will be reviewed here. Reaction of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane with potassium, cesium, or Cs-K-Na alloy in THF gave the results summarized in Scheme II; the observed product was the rearranged anion 15 (product of 1,4 migration of

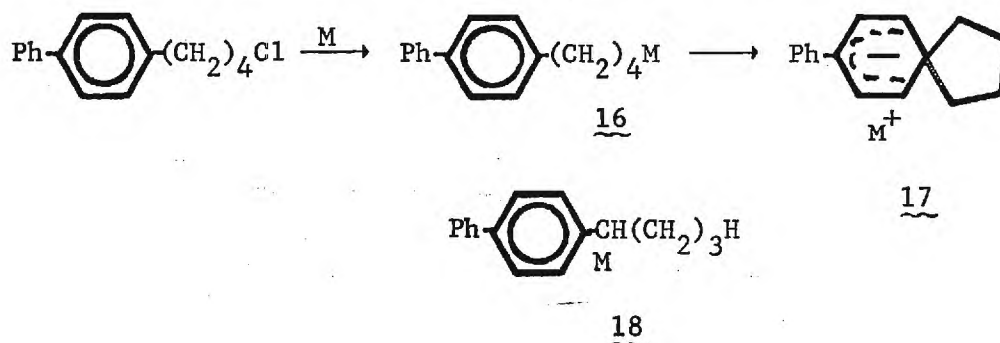
Scheme II



- (4) E. Grovenstein, Jr., S. Akabori, and J.-U. Rhee, *J. Amer. Chem. Soc.*, **94**, 4734 (1972).
- (5) E. Grovenstein, Jr., J.-U. Rhee, *J. Amer. Chem. Soc.*, **97**, 769 (1975).
- (6) E. Grovenstein, Jr. and S. Akabori, *J. Amer. Chem. Soc.*, **97**, 4620 (1975).

p-biphenyl) as deduced from its nmr spectrum and the products of protonation and carbonation. That this rearrangement proceeded by way of the unrearranged organoalkali compound 13 was shown by "trapping" of 13 by proton donors. Also 13 where M = Li was synthesized and shown to be stable to thermal rearrangement; however, the lithium compound 13 rearranged to 15 upon treatment with potassium t-butoxide (most likely due to formation of the corresponding organopotassium compound 13, M = K).

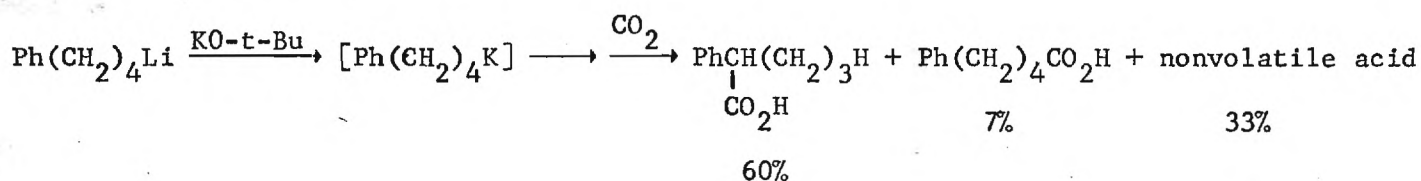
While in the work cited above no direct evidence for the spiro anion 14 as an intermediate or transition state in the 1,4 migration of p-biphenyl was obtained, a strong case can be made for one or the other of these possibilities based on the isolation of the stable spiro anion 17 during reaction of 4-p-biphenylbutyl chloride with potassium, cesium, or Cs-K-Na alloy in THF as shown below. Again the intermediate formation of the unrearranged organoalkali



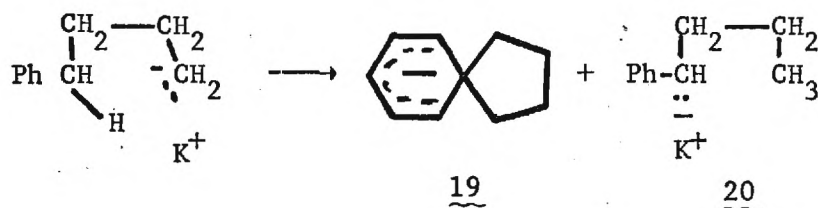
compound 16 was implied by "trapping" experiments with proton donors. No evidence (deuterium-labeling studies) for the spiro anion 17 reopening to give 16 or products derived therefrom was obtained, in contrast to the work reported (see Scheme I) for the lower homolog.

D. [1,4] and [1,5] Rearrangement of Hydrogen in ω-Phenylalkyl Anions.

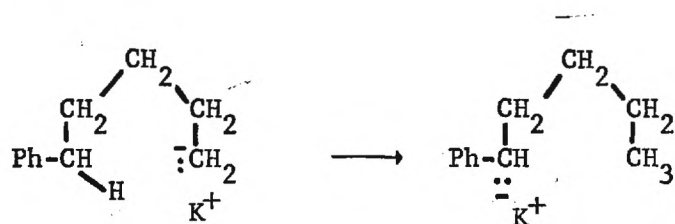
In the reaction of 4-p-biphenylbutyl chloride with cesium alloy at -70° in THF 3% of 1-p-biphenylbutyl anion 18 is formed simultaneously with the spiro anion 17. In contrast the reaction of 4-phenylbutyl chloride with Cs-K-Na alloy under similar conditions gave some 47% of 1-phenylbutyl anion. Similarly reaction of 4-phenylbutyllithium with excess of potassium t-butoxide for 17 minutes at -75° gave after carbonation and gas chromatographic analysis of the methyl esters the results shown below:



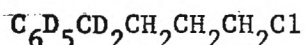
Speculatively the nonvolatile acid may have been derived from the spiro anion 19; anion 20 appears to have come from a [1,4] rearrangement of hydrogen.



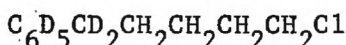
In like manner reaction of 5-phenylpentyllithium with potassium *t*-butoxide for 13 minutes gave, after carbonation, 83% of 2-phenylhexanoic acid, 15% of 6-phenylhexanoic acid, and a negligible amount of nonvolatile acid. The major product 2-phenylhexanoic acid appears to have come from a [1,5] rearrangement of hydrogen.



In order to determine whether the rearrangements of hydrogen in the anions are intra- or inter-molecular processes the deuterium-labeled compounds 21 and 22



21



22

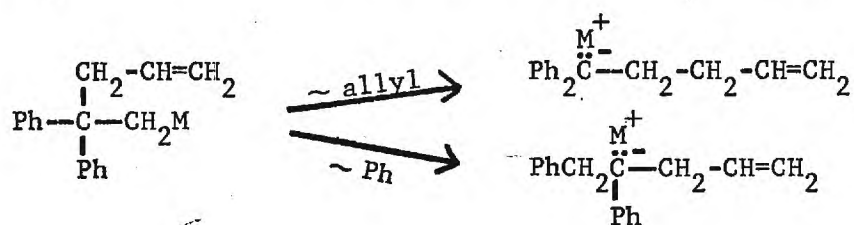
have been prepared. These compounds should be useful also in determining whether or not spirocyclization (*cf* 19) is reversible. The conversion of these labeled chlorides to the corresponding organoalkali compounds is under current investigation.

E. Rearrangement of Benzyl and Phenyl in 2,2,3-triphenylpropyl Anion.

In previous work we studied the rearrangement of 2,2,3-triphenylpropyllithium in tetrahydrofuran at 0° and reported at least 98% 1,2-migration of benzyl⁷. In new work⁸ we have found that under other conditions exclusive 1,2-migration of phenyl rather than benzyl may be obtained. The factors which control the migratory aptitude of groups in this system have been explored in some detail and a theory proposed to explain the results. See our attached Communication (Attachment I). We believe that this work makes an important contribution toward understanding and controlling rearrangements of carbanions. The knowledge gained has already proven useful in a current study of rearrangement of allyl versus phenyl groups in anions (see next section).

F. Rearrangement of Allyl and Phenyl in 2,2-Diphenyl-4-pentenyl Anion.

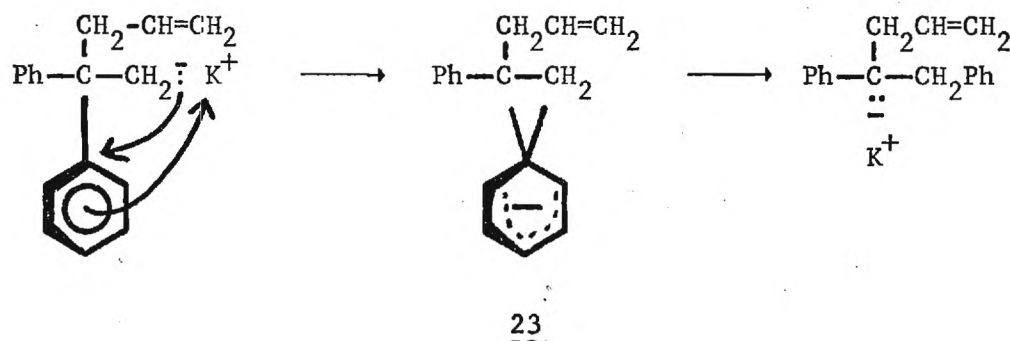
2,2-Diphenyl-4-pentenylalkali compounds have been found to undergo 1,2 rearrangement of either phenyl or allyl groups as shown below:



With M being lithium in THF at -50°, 99% allyl migration and only 1% phenyl migration was observed; however, with M potassium or cesium 67% or 75% phenyl migration respectively was observed (with the remainder allyl migration) in THF at -75°. With M potassium complexed with one mole of 18-crown-6, 86% allyl and 14% phenyl migration was observed in THF at -75°. It is concluded that conditions which favor loose ion pairs (Li^+ , rather than K^+ or Cs^+ , or K^+ complexed with 18-crown-6) favor migration of allyl while conditions which favor tight ion pairs ($\text{Cs}^+ > \text{K}^+ \gg \text{Li}^+$) favor migration of phenyl.

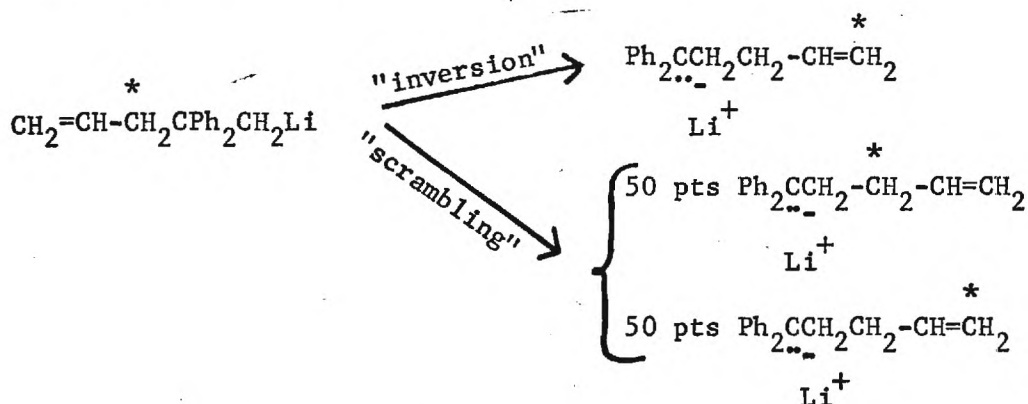
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- (7) E. Grovenstein, Jr., and L. P. Williams, Jr., J. Amer. Chem. Soc., **83**, 2537 (1961).
- (8) E. Grovenstein, Jr., and R. Edward Williamson, J. Amer. Chem. Soc., **97**, 646 (1975).

By analogy with other rearrangements⁸, phenyl migration is believed to proceed in a tight ion pair by way of the intermediate or transition state 23:



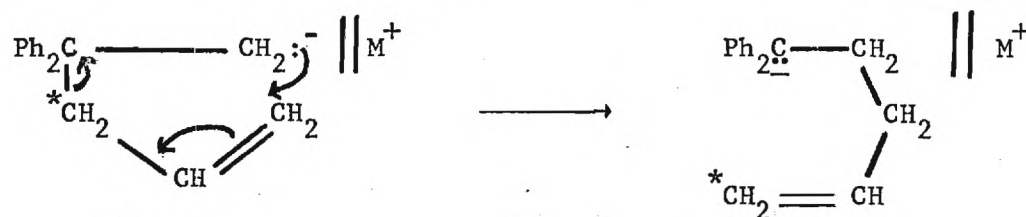
In contrast, allyl migration appears to require extensive cation solvation and hence likely proceeds in a loose ion pair or a free anion.

The detailed mechanism of allyl migration has been studied by use of the labeled compound 2,2-diphenyl-4-pentenyl-3-¹⁴C chloride. The reaction of this chloride with lithium metal in THF at -75° gave 2,2-diphenyl-4-pentenyl-3-¹⁴C lithium which was allowed to undergo rearrangement at 0°, -33° and -50° and gave 65%, 45%, and 33% respectively of "scrambling" with the remainder "inversion" of the allylic terminus:

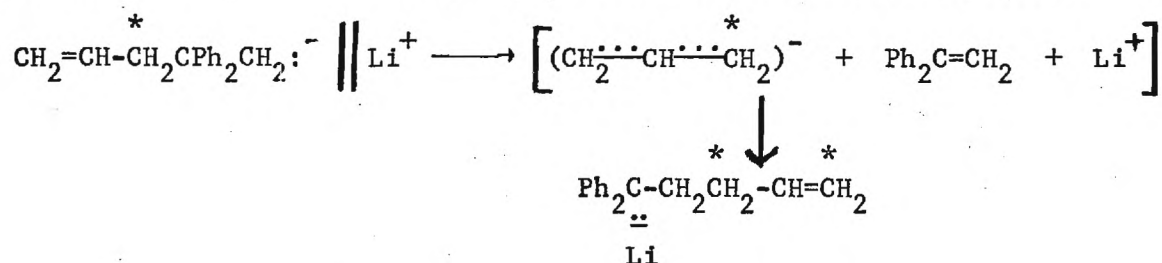


Rearrangement of the same lithium compound at -75° by the addition of five equivalents of a 1:1 complex of potassium tert-butoxide:18-crown-6 ether (which is believed to involve rearrangement of the corresponding potassium compound complexed with 18-crown-6 ether) gave an allyl migration product in which there was exclusively inversion of the allylic terminus. Addition of allyl-¹⁴C-lithium at -75° to 2,2-diphenyl-4-penten-1-yl lithium at -75° with subsequent rearrangement at 0° resulted in only 10% incorporation of ¹⁴C in the product of allyl migration.

Allyl migration is believed to proceed by a duality⁹ of mechanism. The "inversion" mechanism which preponderates at -75° is likely a concerted supra-supra [3,2] sigmatropic rearrangement in a loose ion pair (or free anion):



The "scrambling" mechanism which is favored at 0° is believed to occur in a loose ion pair (or free anion) by an elimination-readdition process:



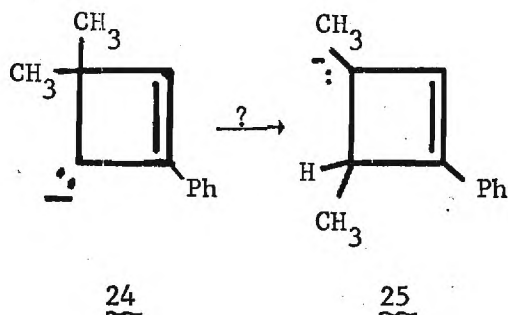
In the first step allyl anion, diphenylethylene, and possibly lithium cation are formed within a solvent cage. A little of the allyl anion (ca 10%) is able to escape from the solvent cage and be replaced in the cage with external allyl anion. Presumably all of the allyl anion (at least 65% at 0°) survives in the cage long enough to undergo several rotations such that the environment about either end of the allyl group becomes equilibrated on a time average before the allyl anion adds to the diphenylethylene within the solvent cage to give the observed product. This mechanism is very similar to that which was proposed earlier for benzyl migration¹⁰.

(9)Cf. J. E. Baldwin and F. J. Urban, Chem. Commun., 165 (1970).

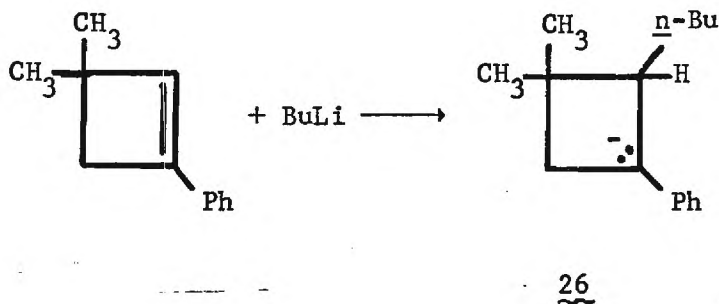
(10) E. Grovenstein, Jr., and G. Wentworth, J. Amer. Chem. Soc., 85, 3305 (1963); 89, 1852 (1967).

G. 4,4-Dimethyl-2-phenyl-2-cyclobutenyl Anion

The 4,4-dimethyl-2-phenyl-2-cyclobutenyl anion 24 is of interest since

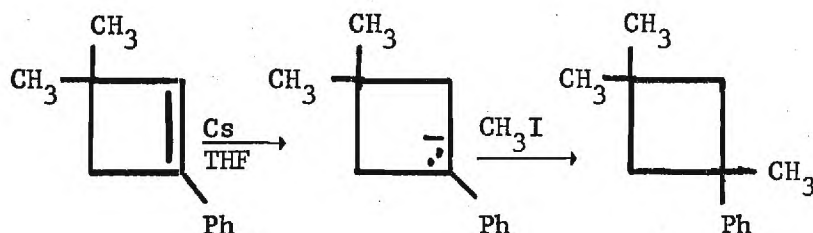


this anion offers an interesting possibility for studying the, as yet, unobserved, migration of methyl in a carbanion, e.g., 24 \longrightarrow 25. Toward this end the hydrocarbon 3,3-dimethyl-1-phenylcyclobutene has been synthesized and reacted with strong bases in hopes of obtaining the desired cyclobutenyl anion 24. To date such attempts have met only with failure. Thus, with n-butyl lithium in pentane activated by tetramethylethylenediamine (TMEDA) at room temperature or by potassium t-butoxide in THF at -55° or in hexane at room temperature only the product 26 of addition of n-butyl anion has been observed. Similarly t-butyllithium in pentane with TMEDA at room temperature gave the corresponding adduct with t-butyl anion. With the weaker



base lithium diisopropylamide in THF at reflux temperature no reaction was observed nor did detectable deuterium exchange occur in presence of D-N(i-Pr)₂.

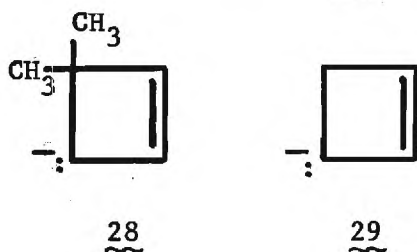
Also, 3,3-dimethyl-1-phenylcyclobutene was found to react with cesium metal in THF to give a red anion; however, methylation of the anion with methyl iodide gave 1,3,3-trimethyl-1-phenylcyclobutane. Thus the red anion had structure 27 rather



27

than the desired structure 24. Reaction proceeded again to eliminate the double bond - this time by addition of electrons and protons from the solvent.

The high reactivity of the double bond in 3,3-dimethyl-1-phenylcyclobutene seems attributable to its styrene-like structure; evidently the reactivity of the double bond is also enhanced by relief of some steric strain in the adduct. What the present experiments leave unanswered is whether or not the desired anion 24 may be too unstable for preparation. This might be the case if the anion is anti-homoaromatic; the related cyclobutenyl cation is thought to be homoaromatic¹¹. Since the stability or instability of an anion such as 24 is of theoretical interest, attempts to make this anion (by alternative routes) will continue. Also effort will be devoted to making the anion 28 and/or 29 without the phenyl group.



PART II. Reactions of Cesium and Cesium Alloys with Aromatic Hydrocarbons and Alkyl Halides.

For some years now we¹² have been studying the reaction of Cs-K and Cs-K-Na alloys with aromatic hydrocarbons and alkyl halides. We have often wondered if

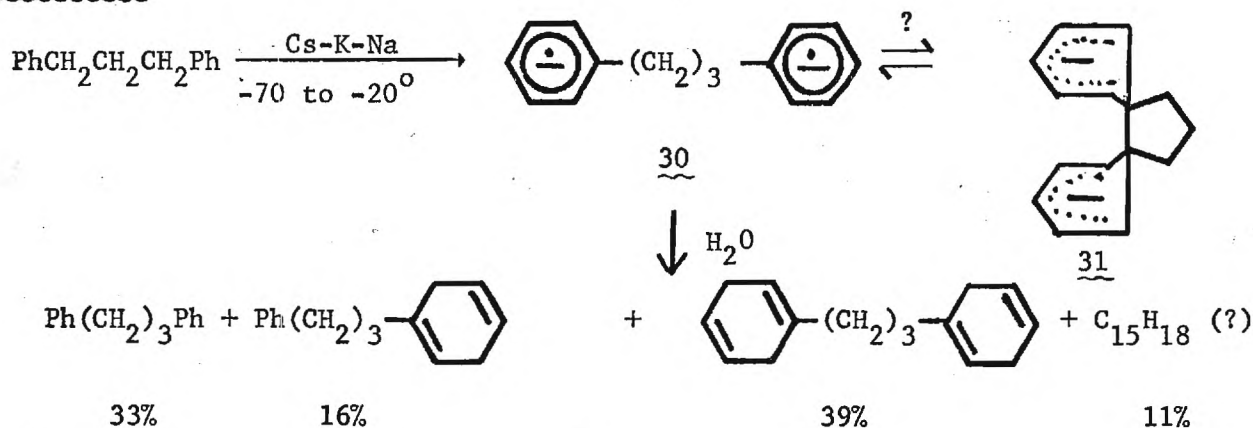
(11) G. A. Olah, J. S. Staral, and G. Liang, J. Amer. Chem. Soc., 96, 6233 (1974).

(12) E. Grovenstein, Jr., J. A. Beres, Y.-M. Cheng, and J. A. Pegolotti, J. Org. Chem., 37, 1281 (1972); E. Grovenstein, Jr., and Y.-M. Cheng, J. Amer. Chem. Soc., 94, 4971 (1972).

the products of these reactions should be described as organocesium or organopotassium (or -sodium) compounds. Much new work has been directed toward answering this question.

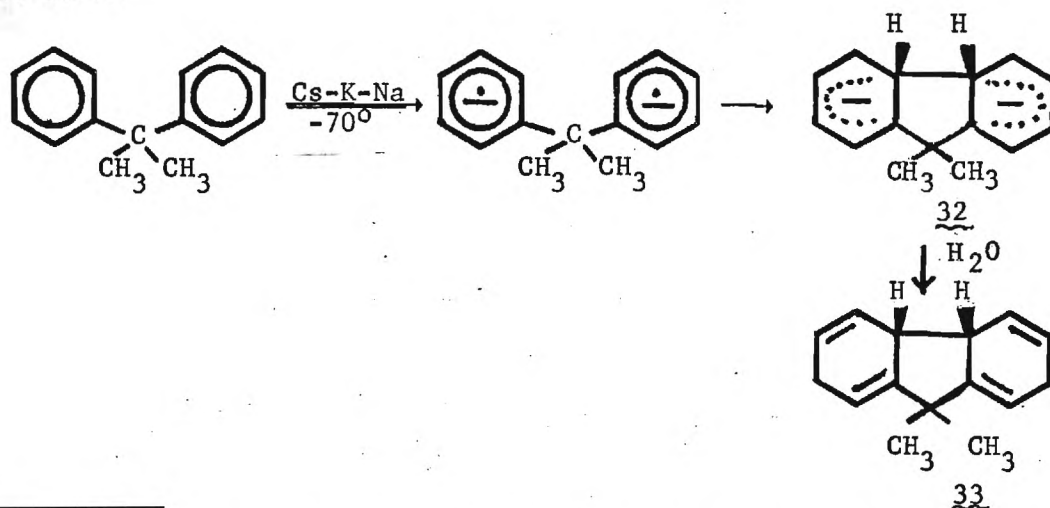
Cs-K-Na alloy has been found to react in THF with 1,3-diphenylpropane to give what appears to be a good yield of the insoluble diradical dianion 30 as deduced from the products of quenching with ice water. While one product remains unidentified, so far no product has been found which would appear to come from the cyclic dianion 31 (see Scheme III).

Scheme III



2,2-Diphenylpropane reacts¹³ with excess Cs-K-Na alloy in THF at -70° to give an intermediate insoluble organoalkali compound which is protonated by water to give cis-9,9-dimethyl-2,4a,4b,7-tetrahydrofluorene 33 likely by Scheme IV. In agreement with this scheme an electron paramagnetic resonance

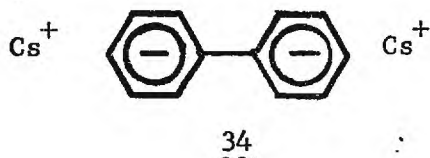
Scheme IV



(13) Thomas H. Longfield, "Reactions of Cesium with Aromatic Hydrocarbons," Ph.D. Thesis, Georgia Institute of Technology, November, 1973; work partially supported by the present grant.

(EPR) study of the intermediate organoalkali compound revealed negligible EPR absorption and hence the intermediate organoalkali compound exists in a singlet state, presumably of structure 32.

Biphenyl reacts¹³ with cesium metal in THF at 36° to give a black precipitate which appears to have the structure 34.



Preliminary work showed that quantitative analysis of ternary alloys of Cs-K-Na was very tedious and, in our hands, inaccurate; in contrast binary alloys of Cs-K could be readily analyzed. By carrying out reactions with excess of liquid binary alloy and analyzing the alloy both before and after reaction with organic substrate the results of Table I were obtained. This table reveals a very selective reaction of all the organic compounds tested with cesium in preference to potassium. The larger standard oxidation-reduction potential of cesium over potassium in aqueous solution evidently pertains also to the solvent tetrahydrofuran; however, while lithium and cesium have the same standard oxidation-reduction potential in aqueous solution, the extensive reaction of 1,3- and 2,2-diphenylpropane with cesium has not been observed with lithium. The ionic radius of cesium¹⁴ (1.69 or 1.86 Å) is about the same as the radius of a benzene ring (1.40 Å out to carbon nuclei, 2.16 Å out to the Pauling single-bond radius of carbon). Evidently cesium forms a very snug, tight ion pair with a benzenide anion or a cyclohexadienyl anion.

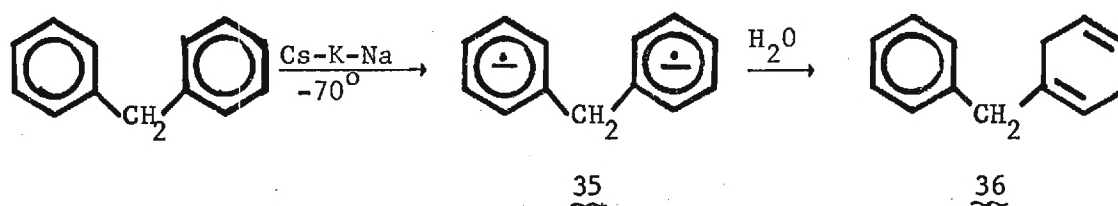
While 2,2-diphenylpropane reacted with Cs-K-Na alloy in THF to give an insoluble product of negligible EPR absorption (see Scheme IV), similar treatment of diphenylmethane gave an intermediate organoalkali compound which possessed strong EPR absorption and, therefore, appears to have the structure 35 (see Scheme V). Protonation of this product by water gave the Birch reduction product 36. The difference in the course of reduction of 2,2-diphenylpropane and diphenylmethane

(14) M. Szwarc, "Ions and Ion Pairs in Organic Reactions," John W. Wiley and Sons, Inc., New York, N. Y., 1972, Vol. 1, p. 3.

TABLE I - Reactions of Organic Compounds with Cs-K Alloy in THF

COMPOUND	TEMPERATURE	COMPOSITION OF ALLOY IN ATOM PERCENT		
		INITIAL	FINAL	CALCULATED*
1,3-Diphenylpropane	-22 to -17°	67.2% Cs 32.8% K	51.7% Cs 48.3% K	52.4% Cs 47.5% K
2,2-Diphenylpropane	-34 to -20°	53.6% Cs 46.4% K	41.1% Cs 58.9% K	39.5% Cs 60.5% K
Biphenyl	27 to 30°	63.7% Cs 36.3% K	53.2% Cs 46.8% K	49.8% Cs 50.2% K
Cyclohexyl Chloride	-20 to -16°	68.0% Cs 32.0% K	53.7% Cs 46.5% K	54.4% Cs 45.6% K

* The calculated values are based on the assumption of 100% reaction of the organic compound and on the basis that each benzene ring in the hydrocarbon or each molecule of alkyl halide reacts with one atom of cesium (no reaction of potassium).

Scheme V

illustrates the unique character of the chemistry of insoluble ionic aggregates wherein the course of the solid state chemistry is likely to be determined by factors such as packing in crystal lattices. Under such conditions steric effects, induced in the present case by replacement of two hydrogen atoms by methyl groups, are likely to play an even more important role than in the chemistry of homogeneous solutions.

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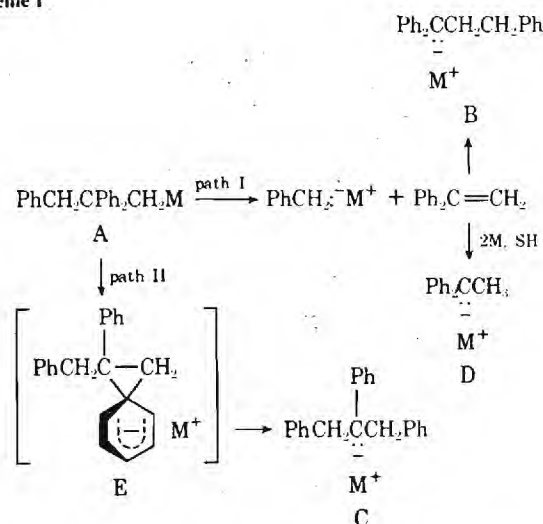
Carbanions. XV. Tight and Loose Ion Pairs in Rearrangements of Organoalkali Compounds¹

Sir:

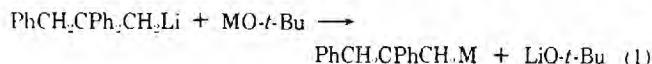
Whereas 2,2,3-triphenylpropyllithium (A), prepared from reaction of 1-chloro-2,2,3-triphenylpropane with lithium at -65 to -75° , has been reported² to rearrange in tetrahydrofuran (THF) at 0° with at least 98% 1,2-migration of benzyl, we now find that reaction of the same chloride with cesium in THF at 65° gives 96% 1,2-migration of phenyl rather than benzyl. In order better to understand the phenomena responsible for such diverse migratory aptitudes, the rearrangement has been studied under widely variable conditions as reported in Table I. Previous work³ has indicated (see Scheme I) that benzyl migration proceeds by elimination of benzyl anion and readdition of this anion to 1,1-diphenylethene to give B (path I) while aryl migration proceeds intramolecularly via a spiro anion to C (path II). In the present work 1,1-diphenylethyl anion (D) has been identified; indeed D is a major product under strongly reducing conditions with solutions⁴ of alkali metals (e.g., potassium plus 18-crown-6 in THF). It is reasonable to suppose that this anion results from reduction of intermediate 1,1-diphenylethylene. The appearance of D along with benzyl anion⁵ constitutes additional evidence for the occurrence of path I.

Examination of Table I reveals that 2,2,3-triphenylpropyllithium does not rearrange at an appreciable rate upon standing in the THF at -75° , even upon addition of 18-crown-6 ether;⁶ however, sodium *tert*-butoxide or better potassium and cesium *tert*-butoxides are effective catalysts, with the product being notably dependent upon the cation present. For a related rearrangement, lithium *tert*-butoxide, unlike potassium or cesium *tert*-butoxides was an ineffective catalyst.⁷ These pronounced cation effects suggest that the cation plays an important role in determining the fate of

Scheme I



the anion and imply that the cation must be geometrically close to the anion during the rearrangement process. This could be understood, for example, if the rearrangement catalyzed by cesium *tert*-butoxide took place in the corresponding organocesium compound; therefore, the following metathetical reaction appears to occur under our conditions



Additional evidence (see Table I) for this metathesis comes from the similar ratio (equal within likely experimental errors) of products of path I to path II observed for the reaction of cesium metal with the chloride at -75° as compared to the reaction of cesium *tert*-butoxide with the organolithium compound at the same temperature.

Table I. Rearrangements of 2,2,3-Triphenylpropyl Alkali Metal Compounds

Conditions	Temp, $^\circ\text{C}$	Products, ^a rel mol %			
		A	B	C	D
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Li}$, 7 hr, THF	-75	100	0	0	0
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Li} + 2(18\text{-crown-6})$, 3.3 hr, THF	-75	100	0	0	0
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Li}$, 30 min, THF	0	0	100	0	0
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Li}$, 3 hr, Et_2O	$+35$	0	0	100	0
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Li} + 2\text{NaO-}t\text{-Bu}$, 30 min, THF	-75	33	58	0	9
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Li} + 2\text{KO-}t\text{-Bu}$, 30 min, THF	-75	0	63	37	0
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Li} + 2\text{CsO-}t\text{-Bu}$, 30 min, THF	-75	0	25	72	3
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Li} + 2\text{KO-}t\text{-Bu} + 2(18\text{-crown-6})$, 30 min, THF	-75	0	100	0	0
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Li} + 2\text{CsO-}t\text{-Bu} + 2(18\text{-crown-6})$, 30 min, THF	-75	20 ^b	77	0	3
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Cl}$, K, THF	$+65$	0	10	90	0
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Cl}$, Cs, THF	$+65$	0	2	96	2
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Cl}$, Cs, ^c THF	-75	0	5	67	28
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Cl} + 2(18\text{-crown-6})$, excess K, THF	-75	0	2	0	98
$\text{PhCH}_2\text{CPh}_2\text{CH}_2\text{Cl} + 2(18\text{-crown-6})$, excess Cs, ^c THF	-75	0	0	<8	>92 ^d

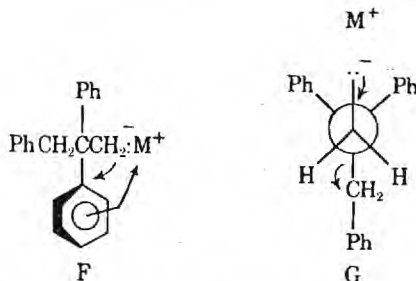
^a Yields are based only on acidic products from carbonation; the entry "0" % means that none was detected by the nmr and glpc techniques used and therefore less than 1 or 2% was present. ^b The reaction is apparently retarded by precipitation of a cesium *tert*-butoxide complex with the 18-crown-6. ^c The organoalkali product was treated with excess mercury to lower activity of cesium (destruction of radical anions) prior to carbonation. ^d The measured ratio of C:D was 8:92 in this run; however, since the ratio of Cs:18-crown-6 was 1.15:1 and the adventitious presence of an impurity caused most of the cesium to react, it is thought that the yield of C would have been reduced if an excess of 18-crown-6 over cesium had been present.

While the present work is to our knowledge the first report¹ of the use of alkali metal alkoxides as catalysts for the rearrangement of organolithium compounds, potassium *tert*-butoxide has been previously reported to activate *n*-butyllithium toward metalation of hydrocarbons such as toluene⁸ and benzene.⁹ Treatment of a heptane solution of *n*-butyllithium with an equimolar amount of potassium *tert*-butoxide is reported⁸ to give a precipitate which has roughly a composition corresponding to a one to one adduct of the alkoxide with the organolithium compound; similar treatment with potassium *l*-menthoxide¹⁰ gives a relatively pure precipitate of *n*-butylpotassium. While the mechanism of potassium alkoxide catalyzed reactions has not been previously elucidated, it has been interpreted as involving formation and facile reactions of either an organopotassium compound^{10,11} or a one to one adduct of organolithium reagent with potassium alkoxide.⁹ The present work favors the former interpretation (eq 1) for reactions in solution in tetrahydrofuran. We find that with a two to one ratio by formula weight of potassium *tert*-butoxide to 2,2,3-triphenylpropyllithium, rearrangement goes to 74% completion in 9 min or 100% ($\pm 3\%$) completion in 30 min, while with a one to one ratio rearrangement goes to only 15% completion in 9 min. Since only one formula weight of alkoxide is required per formula weight of organolithium reagent according to eq 1, the reason why a second formula weight of alkoxide is required for effective catalysis is evidently that it combines with the lithium chloride which is always present in an amount equivalent to the 2,2,3-triphenylpropyllithium in our preparations of organolithium reagent.

In conjunction with the above discussion on the nature of alkoxide ion catalysis, an examination of Table I reveals that the following systems undergo reaction almost exclusively by path I of Scheme I: 2,2,3-triphenylpropyllithium and -sodium in THF at 0 and -75° , respectively; 2,2,3-triphenylpropylpotassium and -cesium 18-crown-6 compounds¹² in THF at -75° , whether prepared *via* the chloride and alkali metal-crown procedure or *via* the lithium compound with alkali metal *t*-butoxide-crown complex. The following undergo rearrangement almost exclusively by path II: 2,2,3-triphenylpropyllithium in ethyl ether at 35° ; 2,2,3-triphenylpropylpotassium and -cesium in THF at 65° . The following undergo reaction in comparable amounts by paths I and II: 2,2,3-triphenylpropylpotassium and -cesium in THF at -75° .

A restatement of these observations is that low temperatures, good solvents for solvating cations, coordination of cations by 18-crown-6, and Li^+ and Na^+ as opposed to K^+ and Cs^+ favor reaction by path I while high temperatures, poorly solvating solvents, absence of good ligands such as 18-crown-6, and large rather than small alkali metal cations favor reaction by path II. The conditions which favor path I are precisely those which favor loose or separated ion pairs while those which favor path II are those which favor tight or contact ion pairs.¹³ Hence, we propose that path I has a transition state resembling a loose ion pair, while path II has a transition state resembling a tight ion pair.

In retrospect it is logical that phenyl migration occurs largely or exclusively in a tight ion pair while benzyl elimination occurs preferentially in a loose ion pair. Thus in the rearrangement leading to the spiro anion, E, the alkali metal cation in the tight ion pair may accompany the anionic center during bridging (see sketch F) such that no great separation of charged centers is necessary at any time for cyclization. In contrast for elimination of benzyl anion from the ion pair, the cleavage reaction gives rise to an alkali metal cation separated from benzyl anion by a molecule of diphenylethylene; this is most obvious if the elimination reaction occurs in the usual *anti-periplanar*¹⁴ conformation



G. In order for elimination of benzyl anion (which possesses a delocalized charge) to occur from a conformation such as G extensive solvation is required to overcome the unfavorable separation of charge in the resulting transition state. Conditions which are ideal for solvating the dipolar transition state are just those required for formation of solvent separated ion pairs. It is tempting to suggest that loose and tight ion pairs are the species which are the immediate precursors respectively for the transition states which resemble loose and tight ion pairs; however, this plausible microscopic picture is not required by thermodynamic arguments.¹⁵

Recently Biellmann and Schmitt¹⁶ have emphasized the importance of solvation in competitive Stevens and Sommelet rearrangements. The intramolecular Sommelet rearrangement was favored by conditions which strongly solvated the cation while the Stevens rearrangement was favored by conditions of weaker solvation.

Acknowledgment. Financial support of this work by the National Science Foundation is gratefully acknowledged.

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ATTACHMENT II

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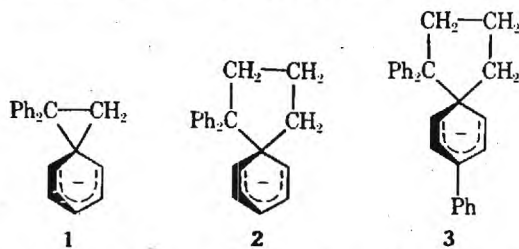
Carbanions. XIV. 1,4 Migration of the *p*-Biphenyl Group in Reactions of 4-Chloro-1-*p*-biphenyl-1,1-diphenylbutane with Alkali Metals¹

Erling Grovenstein, Jr.,* and Jung-Ung Rhee

Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332. Received July 17, 1974

Abstract: 4-Chloro-1-*p*-biphenyl-1,1-diphenylbutane reacts with potassium, cesium, and Cs-K-Na alloy in tetrahydrofuran (THF) to give 4-*p*-biphenyl-1,1-diphenylbutyl anion as deduced from the nmr spectrum of the anion and products of carbonation and protonation. When the reaction with potassium is run in the presence of a small quantity of a sufficiently reactive proton donor such as *tert*-butyl alcohol, the product is 1-*p*-biphenyl-1,1-diphenylbutane or products derived from the latter by subsequent reduction of the *p*-biphenyl group. With sodium in refluxing dioxane the chloride gives 1-*p*-biphenyl-1,1-diphenylbutane containing only some 7% of the rearranged hydrocarbon 4-*p*-biphenyl-1,1-diphenylbutane; with potassium or cesium in the same solvent chiefly the rearranged hydrocarbon is obtained. From these results it is concluded that the chloride reacts with sodium, potassium, and cesium to give 4-*p*-biphenyl-4,4-diphenylbutyl alkali metal compound which is either rapidly protonated or undergoes 1,4 migration of *p*-biphenyl to give the more stable 4-*p*-biphenyl-1,1-diphenylbutyl anion. Reaction of the chloride with excess lithium in THF at -75° gave 4-*p*-biphenyl-4,4-diphenylbutyllithium (4) containing up to 47% of 4-*p*-biphenyl-1,1-diphenylbutyllithium (5). Attempts to induce thermal rearrangement of the lithium compound 4 to 5 resulted primarily in protonation of 4. Addition of the chloride to excess lithium biphenylide in THF at -75° gave 4 containing a little 5; the percentage of 5 decreased as the concentration of lithium biphenylide increased. It is concluded that reaction of lithium biphenylide, and likely of lithium metal, with the chloride initially gives 4-*p*-biphenyl-4,4-diphenylbutyl radical which either rearranges to 4-*p*-biphenyl-1,1-diphenylbutyl radical or is reduced to the lithium compound 4. The lithium compound 4 is readily rearranged to 4-*p*-biphenyl-1,1-diphenylbutyl anion by potassium *tert*-butoxide in THF at -75° . The ease of 1,4 migration of *p*-biphenyl in 4-*p*-biphenyl-4,4-diphenylbutyl alkali metal compounds increases along the series: $\text{Li} \ll \text{Na} \ll \text{K} \text{ or } \text{Cs}$; 1,4 migration is much less facile than analogous 1,2 migration of *p*-biphenyl in carbanions.

Previous investigations² have shown that 1,2 migrations of aryl groups occur readily in organoalkali compounds in ethereal solvents. These rearrangements are believed^{2d,3} to proceed by way of cyclic transition states or intermediates such as **1** from the 2,2,2-triphenylethyl anion. It might be



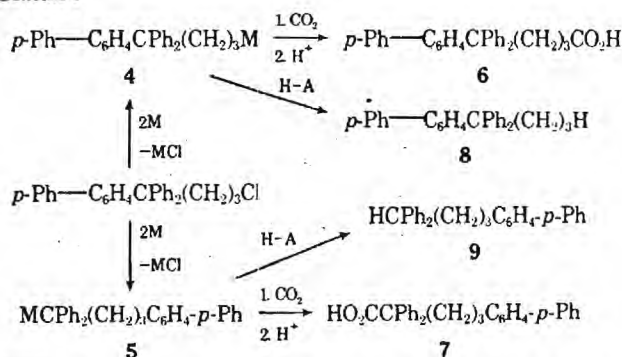
expected that analogous 1,4 migrations of aryl would occur in carbanions, for example, by way of **2** from 4,4,4-triphenylbutyl anion. In fact, reaction of 4-chloro-1,1,1-triphenylbutane with alkali metals under a variety of conditions gave⁴ only minor amounts of products of 1,4 migration of phenyl, and the reactions seemed too complex for study of the mechanism of the observed migration. In the present

work reactions of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane with alkali metals have been studied in hope of avoiding the difficulties encountered in the simpler system, thanks to the expected superior migratory aptitude⁵ of *p*-biphenyl over phenyl in anionic rearrangements. In addition it was thought conceivable that the intermediate **3** might prove stable enough under mild conditions to be detectable by spectroscopic means or by "trapping" experiments.

Results and Discussion

4-Chloro-1-*p*-biphenyl-1,1-diphenylbutane was allowed to react with alkali metals, and the products of reaction were identified after protonation or carbonation to give the corresponding hydrocarbons or carboxylic acids as shown in Scheme I. From reaction with molten potassium in tetrahydrofuran (THF) at 65° , carbonation gave in the acidic fraction only 5-*p*-biphenyl-2,2-diphenylpentanoic acid (**7**), while methanolysis gave 4-*p*-biphenyl-1,1-diphenylbutane (**9**) containing some 1.4% of 1-*p*-biphenyl-1,1-diphenylbutane (**8**). Similar reaction with cesium metal at 65° gave **7** as the only acid from carbonation and a 98:2

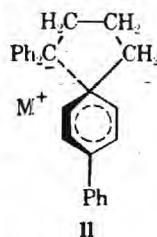
Scheme I



ratio of hydrocarbons 9 and 8 from methanolysis. These results imply that the rearranged organoalkali compound 5 is the major product of these reactions.

In order to attempt to identify likely precursors of 5 such as the unrearranged organoalkali compound 4 or the half-way rearranged spirocyclic anion 3, the reaction of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane was run with the minimum melting alloy⁴ of cesium, sodium, and potassium in THF at -75° . The products of carbonation and hydrolysis, even after a reaction time of only 2 min, again proved to be primarily 7 and 9, derived from the rearranged organoalkali compound 5.

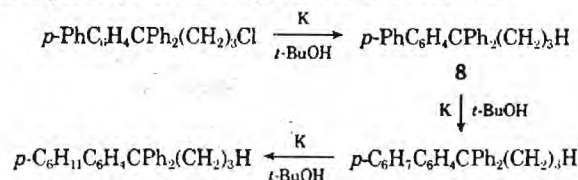
The structure of the dark red carbanion from reaction of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane with Cs-K-Na alloy was further confirmed by its nmr spectrum in THF which had absorption by the protons of the *p*-biphenyl group at δ 7.17, much like the absorption reported^{2f} (δ 7.19) for the aromatic protons in *p*-biphenylethane, while the aromatic protons of the diphenylmethyl anion moiety absorbed as a doublet at δ 6.93 (ortho hydrogens), a triplet at δ 6.70 (meta hydrogens), and a triplet at δ 5.84 (para hydrogens). The latter absorptions are similar to those reported⁶ for triphenylmethyl lithium (δ 7.31 (d, ortho H), 6.52 (t, meta H), 5.96 (t, para H)) and diphenylmethyl lithium (δ 6.52 (ortho and meta H) and 5.65 (para H)) in THF and are very different from those^{1b} of 9-phenylspiro[4.5]deca-6,9-dienyl anion. The nmr spectrum of the present dark red anion is therefore fully in agreement with structure 5. The failure to observe products of carbonation and protonation which retain the carbon skeleton of the spiro anion 3 is accordingly due to the absence of this carbon skeleton in the products, not to an artifact in the chemical reactions of the anion. Any nonclassical interaction of the diphenylmethyl anionic center of 5 with the biphenyl group as implied by the dashed line in structure 11 must be small or nonexistent.



In further experiments to attempt to trap intermediates in the reaction of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane with alkali metals, the reaction was run in the presence of various proton donors as given in Table I. The reactions with potassium in THF at reflux temperature are listed according to the expected order of proton donating ability of the proton source. With no added proton donor or in the presence of *n*-butylamine, the hydrocarbon produced (after addition of methanol) is predominantly the rearranged hydrocarbon 9. In the presence of triethylcarbinol, increased amounts of the nonrearranged hydrocarbon 8 are produced.

In the presence of the still more reactive proton donor *tert*-butyl alcohol, only products of nonrearranged carbon skeleton are produced.

The reduction of the chloride in THF in the presence of alcohols is complicated by reduction of the biphenyl group to dihydro and hexahydro (cyclohexyl) derivatives. Analysis of the reaction mixture in the experiment with *tert*-butyl alcohol showed that the yield of hydrocarbon 8 reached a maximum of 18% after the third incremental addition of potassium and *tert*-butyl alcohol but that this product largely disappeared with continued reduction with excess potassium. The final product, after eight incremental additions of potassium and *tert*-butyl alcohol, consisted of 3% of 8, 90% of 1-*p*-cyclohexylphenyl-1,1-diphenylbutane, and 6% of a dihydro derivative of 8 of likely structure, 1-*p*-(1,4-dihydrophenyl)phenyl-1,1-diphenylbutane. The reduction sequence, therefore, appears to be as follows.



Phenylcyclohexane has been reported⁷ as a minor product of alcoholysis of the biphenyl adducts of lithium and sodium. The present procedure appears to have synthetic merit as a general method for the reduction of a 4-alkylbiphenyl to a 4-cyclohexyl-1-alkylbenzene.

In refluxing dioxane 2-chloro-1,1,1-triphenylethane reacts^{2a} readily with sodium to give the rearrangement product, 1,1,2-triphenylethylsodium. Accordingly these same conditions have been applied to the reaction of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane with sodium. Since in a preliminary reaction only the unrearranged hydrocarbon 8, but no carboxylic acid, was obtained on carbonation, the reaction was repeated (see Table I) with dioxane which was treated with *n*-butyl chloride and excess sodium just before the addition of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane, in order that the *n*-butylsodium formed might scavenge any impurities in the dioxane. This pretreatment resulted in the formation of some 8% of the rearranged hydrocarbon 9 along with 92% of 8. Another run in which the dioxane was stirred vigorously and finally distilled from molten potassium before pretreatment with *n*-butyl chloride gave about the same ratio of 9 to 8 in the final product. The high yield of nonrearranged hydrocarbon 8 in these reactions suggests that dioxane is functioning as a proton donor⁸ to an intermediate carbanion much as *tert*-butyl alcohol functioned in the previous reactions with potassium in THF; however, the reactions with sodium in dioxane are not complicated by reduction of the biphenyl group.

In contrast to the reaction with sodium, reaction of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane with potassium in dioxane gave, after carbonation, primarily the rearranged hydrocarbon 9, containing none of the nonrearranged hydrocarbon 8, and only a trace (0.4%) of the rearranged carboxylic acid 7. Evidently organopotassium compound 5 is nearly completely protonated by dioxane at 101° in less than 20 min to give hydrocarbon 9. By way of comparison 1,1,2-triphenylethylsodium is somewhat less than half protonated by dioxane at 101° in some 45 min.^{2a} With the present chloride, rearrangement occurs much more readily with potassium than with sodium.

In order to examine further the effect upon the product composition of varying the alkali metal, reaction with cesium was studied (Table I). Because of the ready cleavage of dioxane by cesium metal (*cf.* the slow cleavage of dioxane

Table I. Products from Reaction of 4-Chloro-1-*p*-biphenyl-1,1-diphenylbutane (RCl) with Alkali Metals in the Presence of Various Proton Donors

RCl, mmol	Metal (mg-atom)	Temp, °C	Proton donor added		Products, ^a % ^b				
			A-H	(mmol)	9	9 + 6H	8	8 + 2H	8 + 6H
In Tetrahydrofuran									
2.6	K (7.1)	65	None		98	0	1.4	0	0 ^{c,d}
2.7	K (5.8)	65	<i>n</i> -BuNH ₂	(12.5)	95	0	4.5	0	0 ^c
2.3	K (7.1)	65	(CH ₃ CH ₂) ₃ COH	(6.8)	43	7	5.5	0	7 ^e
0.72	K (5.8)	65	CH ₃ COCH ₃	(9.5)	0	0	3.3	0	5.4 ^e
2.54	K (5.9)	65	(CH ₃) ₃ COH	(14.2)	0	0	4.0	1.8	11 ^e
	K' (3 × 6.5)	65	(CH ₃) ₃ COH	(3 × 6.2)	0	0	14.6	5.0	65 ^e
In Dioxane									
4.6 ^g	Na (120)	101	None		8	0	92	0	0
5.3 ^g	Na (99)	101	None		5.3	0	86	0	0 ^h
5.1 ^g	K (123)	101	None		77 ⁱ	0	0	0	0
2.5	Cs (38)	40	None		89	1.3	3.6	0	0 ^{e,j}
2.5	Cs (38)	30 ^k	None		14	82	0	0	3.6

^a Excess methanol (or ethanol) was added to all analytical samples at the conclusion of the reaction. The products are: 9, 4-*p*-biphenyl-1,1-diphenylbutane; 9 + 6H, 4-*p*-cyclohexylphenyl-1,1-diphenylbutane; 8, 1-*p*-biphenyl-1,1-diphenylbutane; 8 + 2H, likely structure, 1-*p*-(1,4-dihydroxyphenyl)phenyl-1,1-diphenylbutane; 8 + 6H, 1-*p*-cyclohexylphenyl-1,1-diphenylbutane. ^b The area per cent yield of volatile products are listed; see footnote. ^c Also 0.15% of *p*-biphenyldiphenylmethane (10) was observed. ^d Also 0.8% of an unknown of 0.52 times the retention time of 10 was observed. ^e The remainder was unreacted chloride. ^f The reaction mixture from the first reaction in the presence of *tert*-butyl alcohol was treated with three successive portions of potassium and *tert*-butyl alcohol to give the final product shown. ^g *n*-Butyl chloride was added prior to addition of RCl. ^h The other products were 6% of 10 and 2% of unknown of 1.2 times the retention time of 10. ⁱ This product was obtained in the neutral fraction from carbonation; for the other products see the Experimental Section. ^j The absolute mole per cent yield of products was 3.3% of 8, 1.2% of 9 + 6H, 81% of 9, and 6.6% of unreacted RCl. ^k The temperature rose to 37° after addition of RCl.

by Na-K alloy at 101° to give ethylene and alkali metal salt of ethylene glycol⁸, the reaction had to be studied at temperatures of 30–40°. At 40° where the excess of cesium was destroyed by cleavage of dioxane, the products were chiefly the rearranged hydrocarbon 9 and some 3% yield of unrearranged hydrocarbon 8. In a run initiated at 30° with excess of cesium present the product was about the same mixture of 8 and 9 but this time reduced to their hexahydro(*p*-cyclohexylphenyl) derivatives. This reaction illustrates the superior reducing power toward benzenoid rings of cesium⁴ over sodium and potassium and the use of dioxane as a proton source in Birch-like⁹ reductions.

Since 1,2 migrations of aryl groups have been observed in rearrangements of many organolithium compounds,^{2,3} frequently upon warming THF solutions of such lithium compounds to 0°, corresponding 1,4 migration of *p*-biphenyl has been sought in reactions of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane with lithium. Reaction of this chloride with a 15:1 ratio of gram atoms of lithium to moles of chloride at –70 to –75° gave in four runs upon hydrolysis a 75:25 mixture (±6%) of nonrearranged 8 to rearranged 9 hydrocarbons or upon carbonation a similar ratio of acids 6:7. Attempts to induce further rearrangement by storing the organolithium reagent at –11° for 8 hr gave only a 2% (if any) increase in the amount of rearrangement as judged by the products of protonation or, after storage at 0° for 4 hr, a 4% increase in rearrangement. Since most of the organolithium reagent, according to the results of carbonation, was protonated by solvent after such long periods of storage, attempts to induce appreciable thermal rearrangement of 4-*p*-biphenyl-4,4-diphenylbutyllithium (4) are deemed to be impractical. To be sure, the organolithium reagent which better survived such thermal treatment was the more stable rearranged organolithium compound 5.

In these runs a large excess of lithium metal over halide was used in the preparation of the organolithium compound in order to give a high yield of lithium reagent in a few hours at the low temperatures of the present preparations. When the ratio of gram atoms of lithium metal to moles of chloride was increased to about 80:1, the product in four runs after methanolysis consisted of a 53:47 (±1%) ratio of nonrearranged 8 to rearranged 9 hydrocarbons. The in-

crease in extent of rearrangement with increase in the ratio of lithium metal to halide is notable and proved to be reproducible under our conditions. Also the very large amount of rearrangement observed during preparation of the organolithium reagent from the present chloride appears to be without precedent. It has been previously reported¹⁰ that 6.4% of the rearranged product 1,1-dimethyl-2-phenylethyllithium is present in the 2-methyl-2-phenylpropyllithium prepared from the reaction of neophyl chloride with lithium metal in THF at –70°. Since 4-*p*-biphenyl-4,4-diphenylbutyllithium (4), once prepared, undergoes little if any rearrangement upon warming to 0° for several hours, it is clear that the large amount of 4-*p*-biphenyl-1,1-diphenylbutyllithium (5) produced during preparation of 4 at –70 to –75° cannot result from rearrangement of the organolithium compound 4. A similar conclusion applies to the rearranged product from reaction of neophyl chloride with lithium.

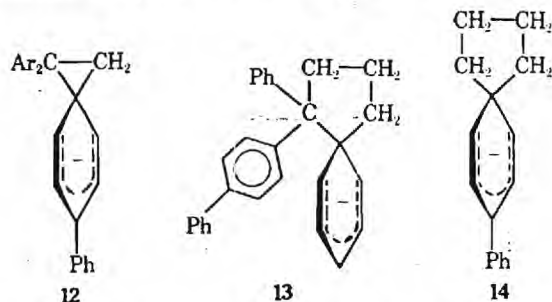
In an attempt to gain further insight into the reaction of lithium metal with 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane, we have studied the reaction of the chloride with lithium biphenylide. Addition of the chloride to an excess of 0.03 *M* lithium biphenylide in THF at –75° gave upon methanolysis a 92:8 ratio of hydrocarbons 8:9 or upon carbonation a similar ratio of acids 6:7. The yield of 6 based upon starting chloride was 63%. Other experiments showed that if the initial concentration of lithium biphenylide was higher (0.24 *M*) the ratio of hydrocarbons 8:9 from methanolysis was 98:2 while if the concentration was lower (0.011 *M*) this ratio was 88:12. In a similar reaction of neophyl chloride with lithium biphenylide, carbonation of the product gave a 99:1 ratio of 3-methyl-3-phenylbutanoic acid to 2,2-dimethyl-3-phenylpropanoic acid or a 76% yield of the former acid based on the amount of starting neophyl chloride (or a 92% conversion based upon the neophyl chloride consumed). Under appropriate conditions, therefore, *lithium biphenylide can react with organic chlorides*, which are prone to give lithium reagents of rearranged structure with lithium metal, *to give organolithium compounds of unrearranged structure in high yields*. The synthetic utility of lithium biphenylide for the preparation of organolithium compounds from organic chlorides seems not to have been

previously noted, though Eisch¹¹ reported a 70% yield phenyllithium from reaction of fluorobenzene with reportedly a 2:1 adduct of lithium with biphenyl in THF at -10° . Other synthetically useful reactions of alkali metal adducts of aromatic hydrocarbons have been reported by Bank and co-workers.¹²

Having demonstrated that 4-*p*-biphenyl-4,4-diphenylbutyllithium does not undergo any appreciable thermal rearrangement in THF by itself, we next sought reaction conditions which might facilitate such rearrangement. The report¹³ that organopotassium compounds can sometimes be synthesized by the reaction of potassium alkoxides with organolithium compounds in hydrocarbon solvents, or that very reactive adducts^{13,14} of organolithium compounds with potassium alkoxides are formed, encouraged us to look for catalysis of the rearrangement of 4-*p*-biphenyl-4,4-diphenylbutyllithium by potassium *tert*-butoxide in tetrahydrofuran. Addition at -75° of a THF solution of about two formula weights of potassium *tert*-butoxide to a preparation of 4-*p*-biphenyl-4,4-diphenylbutyllithium containing one formula weight of organic and inorganic lithium compounds resulted in an immediate intensification of color. Carbonation after 6 min gave an acidic product containing the rearranged acid 7 (49% yield) but none of the nonrearranged acid 6. Whereas the initial organolithium reagent on methanolysis gave 63:37 ratio of nonrearranged 8 to rearranged 9 hydrocarbons, after addition of potassium *tert*-butoxide this ratio became 32:68. From these results it is evident that potassium *tert*-butoxide has brought about a ready rearrangement of 4-*p*-biphenyl-4,4-diphenylbutyllithium (4) to rearranged organoalkali compound 5.

Conclusions

Reaction of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane with potassium, cesium, or Cs-K-Na alloy tetrahydrofuran results in a very facile 1,4 migration of *p*-biphenyl with no evident 1,4 migration of phenyl. This highly selective 1,4 migration of *p*-biphenyl is similar to the reported^{3b} exclusive ($>98.6 \pm 0.4\%$) 1,2 migration of *p*-biphenyl as opposed to *m*-biphenyl in 2-*m*-biphenyl-2,2-bis(*p*-biphenyl)ethylolithium. The product of the present rearrangement is 4-*p*-biphenyl-1,1-diphenylbutyl anion (5) as deduced both from its products of protonation and carbonation. Since the 1,2 migration of *p*-biphenyl in 2-*m*-biphenyl-2,2-bis(*p*-biphenyl)ethylolithium is believed to occur in an anion by way of a spirocyclic transition state or intermediate 12, it is attractive to postulate a similar inter-



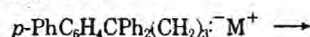
mediate, 3, for the present 1,4 migration of *p*-biphenyl. The formation of such an intermediate would be in agreement with the observed greater migratory aptitude of *p*-biphenyl over phenyl since in 3, unlike in the intermediate 13 for migration of phenyl, the *p*-phenyl group should provide significant stabilization by further delocalizing the charge on the anion. The analogy of 1,4 to 1,2 migrations of aryl groups in anions is weakened by the observation in the present work that 4-*p*-biphenyl-4,4-diphenylbutyllithium does not undergo appreciable rearrangement under thermal

conditions which suffice for effecting related 1,2 rearrangements of organolithium compounds.

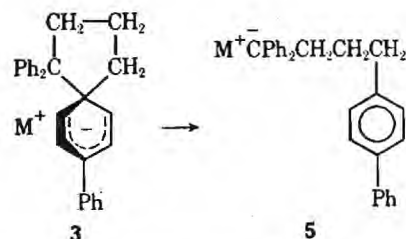
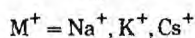
An alternative explanation for the rearrangement observed during reaction of potassium, cesium, or Cs-K-Na with 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane is that the rearrangement occurs in an intermediate free radical. Indeed hitherto unknown cases¹⁵ of 1,4 and 1,5 migrations¹⁶ of aryl groups in free radicals have been reported since the present work was initiated. In order to establish whether or not formation of organoalkali compound 4 precedes rearrangement, 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane was allowed to react with potassium in THF in the presence of various proton donors, the results (Table I) show that the amount of rearrangement in the hydrocarbon products decreased as the expected effective acidity of the proton donor increased. In particular, in the presence of *tert*-butyl alcohol all of the products are of unrearranged carbon skeleton. Since alkyl radicals are very similar to hydrogen atoms in their rate of abstraction of hydrogen atoms from organic compounds and since hydrogen atoms abstract hydrogen from THF more than 150 times more readily than from *tert*-butyl alcohol,¹⁷ the intermediate trapped by addition of small amounts of *tert*-butyl alcohol in the present experiments must be the organopotassium compound 4 rather than the corresponding free radical.

Since, therefore, formation of the organopotassium compound precedes rearrangement, we believe that the rearrangement with potassium and likely also that with sodium, cesium, and Cs-K-Na alloy takes place in the ionic organoalkali compound 4 (see Scheme II). The inability in the

Scheme II



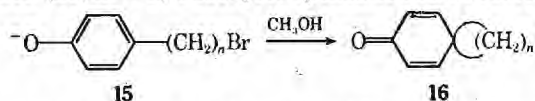
4



present work to detect the presence of the supposed spirocyclic intermediate 3 even at -75° must be attributed to a very facile ring opening of 3 to give 5. This interpretation has been confirmed by reaction^{1b,18} of cesium or potassium with 4-chloro-1-*p*-biphenylbutane in THF to give the stable spiro anion 14.

An interesting observation in the present work is the slow rate of rearrangement (k_R) of 4-*p*-biphenyl-4,4-diphenylbutyllithium (4) compared to the rate of protonation (k_H) of this organosodium compound by dioxane at 101° ; the relative rate k_R/k_H equals about 0.08. In contrast the corresponding relative rate^{2a} k_R/k_H for 2,2,2-triphenylethylsodium in dioxane is 4.5. In this comparison the former organosodium compound undergoes 1,4 migration of *p*-biphenyl while the latter compound undergoes 1,2 migration of phenyl. Since 2-*m*-biphenyl-2,2-bis(*p*-biphenyl)ethylolithium^{3b} at 0° undergoes 1,2 migration of *p*-biphenyl to the extent of at least $98.6 \pm 0.4\%$, the *p*-biphenyl group undergoes 1,2 migration more than 35 times (after statistical correction) more readily than the *m*-biphenyl; a similar or greater ratio should apply to the relative rate of migration of *p*-biphenyl vs. phenyl. From such considerations it is estimated that the relative rate of *p*-biphenyl migration to protonation (k_R/k_H) for 2-*p*-biphenyl-2,2-

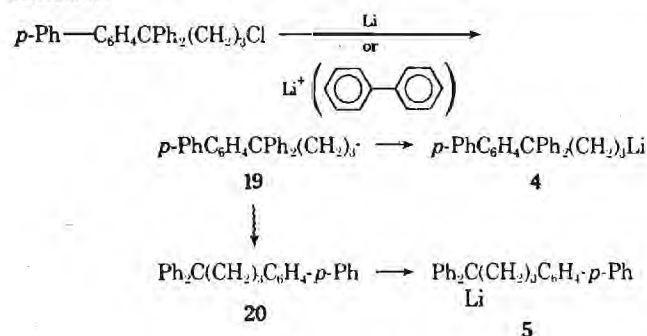
diphenylethylsodium is greater than 157 in dioxane at 101°. If k_H for 2-*p*-biphenyl-2,2-ethylsodium is the same as k_H for 4-*p*-biphenyl-4,4-diphenylbutylsodium within a factor of two, then it is estimated that the rate of 1,2 migration of *p*-biphenyl in the former compound exceeds the rate of 1,4 migration of *p*-biphenyl in the latter by more than 1000-fold. By way of comparison it has been estimated¹⁹ that 2-*p*-hydroxyphenylethyl bromide in the form of its anion (**15**, $n = 2$) undergoes cyclization to **16** some 1100



times more readily than the anion (**15**, $n = 4$) of 4-*p*-hydroxyphenylbutyl bromide. In the case of cyclization of ω -aminoalkyl chlorides, bromides, and nitrates, however, the five-membered heterocycle is formed 10^2 to 10^4 times more rapidly than the three-membered heterocyclic amine.^{19a,20} The factors relating to the ease of formation of various ring sizes have frequently been discussed but are not generally well understood.^{19,20} For the present rearrangements of carbanions, it seems likely that the rearrangement has an early transition state (*cf.* the Hammond²¹ postulate for reactive intermediates) and therefore that the strain in formation of the three-membered ring is not well-developed in the transition state and thus that the "proximity"²² of aryl to carbanionic center governs the relative ease of cyclization.

Another interesting observation in the present work (see Table I) is that the rate of rearrangement of 4-*p*-biphenyl-4,4-diphenylbutyl alkali compound relative to the rate of protonation of the unrearranged organoalkali compound by dioxane, k_R/k_H , is much larger for potassium (>80) than for sodium (0.08) at 101°. Also the value for cesium (25) at 40° is near that of potassium. While these relative rate ratios doubtlessly reflect the effect of the alkali metal cation on both the rate of protonation and the rate of *p*-biphenyl migration, we think the larger effect is on the latter rate; large alkali metal cations evidently favor migration of aryl groups. In this regard our inability to observe appreciable rearrangement of 4-*p*-biphenyl-4,4-diphenylbutyllithium in the much less acidic solvent THF at 0° is of interest ($k_R/k_H < 0.07$). Hence it appears that the order of ease of rearrangement of 4-*p*-biphenyl-4,4-diphenylbutyl alkali metal compounds vs. their protonation by solvent increases rapidly along the series: Li << Na << K, Cs.

While 4-*p*-biphenyl-4,4-diphenylbutyllithium itself did not rearrange appreciably in THF under any of the conditions investigated, nevertheless, samples of 4-*p*-biphenyl-4,4-diphenylbutyllithium which were prepared by reaction of the corresponding chloride with lithium metal always contained large amounts of the rearrangement product, 4-*p*-biphenyl-1,1-diphenylbutyllithium. A possible explanation is that the initial product of the reaction of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane on the surface of lithium metal is the corresponding radical **19** (Scheme III) which in Scheme III



part is free enough from the metal surface to undergo 1,4 migration of *p*-biphenyl. Reduction of the radicals **19** and **20** with lithium then gives the observed products. Related 1,4-migrations of aryl groups in free radicals are known^{15,16} and analogous explanations have been advanced to explain the 1,2 migration of phenyl during reduction of neophyl chloride with magnesium²³ and lithium¹⁰ or at a cathode.²⁴ Similar mechanisms have also been proposed to account for racemization during the corresponding reactions of 1-halogeno-1-methyl-2,2-diphenylpropane.²⁵ While the proposed mechanism appears reasonable, it does not readily explain why the percentage of rearrangement increases with increase in the ratio of lithium metal to chloride. Perhaps only on certain portions of the surface of the lithium metal are the radicals free enough to rearrange and that the quantity of such surfaces increases with the amount of lithium metal used. Alternatively other mechanisms could be proposed; thus the rearrangement might be induced by traces of impurities in the lithium metal.

As a test for the plausibility of the mechanism of Scheme III for reduction by lithium metal, reduction of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane by lithium biphenylide in THF has been studied. This alkali metal adduct of biphenyl like other such alkali metal adducts of aromatic hydrocarbons²⁶ should function as a one-electron-transfer reagent and, therefore, upon reaction with the chloride afford the radical **19**. The subsequent fate of **19** should depend upon the concentration of lithium biphenylide in the immediate surroundings. We find that as the initial concentration of the lithium biphenylide to which the chloride is added varied from 0.011 to 0.24 *M* the percentage rearrangement decreased from 12 to 2%. This observation is in agreement with Scheme III which requires that as the concentration of lithium biphenylide increases the amount of rearrangement of **19** to **20** should decrease because of competitive reduction of **19** to the corresponding organolithium compound **4**. Evidently in the present experiments lithium biphenylide is a more effective "trap" for the intermediate radical **19** than is lithium metal; consequently *lithium biphenylide is preferable to lithium metal* for the preparation of 4-*p*-biphenyl-4,4-diphenylbutyllithium from the corresponding chloride.²⁷

Whereas 4-*p*-biphenyl-4,4-diphenylbutyllithium itself does not undergo appreciable thermal rearrangement in THF under conditions sufficiently vigorous to destroy most of the lithium reagent by extraction of protons from the solvent, addition of potassium *tert*-butoxide to the reagent brings about very ready rearrangement at -75°. This result is most readily explained if the corresponding organopotassium compound¹³ is formed since, as we have demonstrated above, the organopotassium compound rearranges much more readily than the organolithium compound. The present example appears to be the first report of the use of a potassium alkoxide to induce the rearrangement of an organolithium compound; subsequent work²⁸ has demonstrated that sodium, potassium, and cesium, but *not* lithium *tert*-butoxides greatly accelerate the rearrangement of suitable^{2,3,4} organolithium compounds.

Experimental Section²⁹

Proton nmr spectra were recorded on a Varian A-60 nmr spectrometer using tetramethylsilane as an internal standard unless otherwise specified. Mass spectra were run upon either a Varian M-66 or a Hitachi (Perkin-Elmer) RMU-7L mass spectrometer; exact mass determinations were made with the latter instrument.

p-Biphenyldiphenylchloromethane was prepared by the procedure of Lichtin and Glazer.³⁰ *p*-Biphenyldiphenylmethane (**10**), mp 110–112° (lit.³¹ mp 111°) was prepared in 23% yield (based on *p*-bromodiphenyl) by coupling¹² *p*-biphenylmagnesium bromide

with benzhydryl bromide in ether-benzene solution; 1,1,2,2-tetra-phenylethane was formed as a by-product. Cesium metal (99.9+%) was obtained from MSA Research Corporation in sealed glass ampoules. Dioxane was Fisher Scientific Co. certified ACS grade and was purified by treatment with hydrochloric acid and then sodium according to a published procedure.³³ Lithium metal (0.05% Na max) was from Lithium Corporation of America. Methyl 4-*p*-biphenylbutanoate³⁴ (bp 177° at 0.2 Torr; lit³⁵ bp 212–215° at 3 Torr) was prepared by esterification of 4-*p*-biphenylbutanoic acid³⁶ with methanol. Potassium and sodium were Baker reagent grade. Tetrahydrofuran (THF) was Baker reagent grade dried over sodium wire and then distilled from sodium aluminum hydride immediately before use.

Neophyl chloride was prepared by the procedure of Whitmore and coworkers.^{37,38} 2,2-Dimethyl-3-phenylpropanoic acid (mp 57.0–58°, reported³⁹ mp 57°) was prepared³⁸ in 10% yield by carbonation of the Grignard reagent from 2-benzyl-2-chloropropane; this acid upon 50/50 admixture with 3-methyl-3-phenylbutanoic acid melted below room temperature. 3-Methyl-3-phenylbutanoic acid (mp 56–58°, reported⁴⁰ 57.5–58.5°) was prepared by oxidation of 4-methyl-4-phenyl-2-pentanone⁴⁰ with potassium hypochlorite according to a general procedure.^{38,41}

4-Chloro-1-*p*-biphenyl-1,1-diphenylbutane. *p*-Biphenyldiphenylmethylsodium was prepared from 112 g (0.315 mol) of *p*-biphenyldiphenylchloromethane with powdered sodium amalgam (13.3 g of Na, 546 g of Hg) in 1 l. of anhydrous ether according to the general procedure used for preparation of triphenylmethylsodium.⁴² One-fifth of the *p*-biphenyldiphenylmethylsodium was removed for synthesis of 1-*p*-biphenyl-1,1-diphenylbutane (see below) and the remainder was siphoned from the mercury at room temperature into 500 ml of 1-bromo-3-chloropropane under a nitrogen atmosphere. The solution, after standing overnight, was filtered through a sintered glass funnel and the filtrate was concentrated *in vacuo* to a yellow viscous oil. The oil was dissolved in petroleum ether (bp 30–60°) and the solution was stored at refrigerator temperature for 2 days. An oily material was deposited. The solution was separated from the oil by decantation; the solution was evaporated to dryness *in vacuo* and the residue was recrystallized successively from *n*-heptane and then acetone. Colorless crystals (47 g, 47% yield), mp 97.5–100°, were obtained. The analytical sample after recrystallization from acetone, ethanol, and finally *n*-heptane had mp 99.3–100.2° and nmr (CCl₄) δ 7.25 (19 H, m), 3.32 (2 H, t, *J* = 6.0 Hz), 2.72 (2 H, t, *J* = 8.0 Hz), and 1.58 (2 H, m).

Anal. Calcd for C₂₈H₂₅Cl: C, 84.72; H, 6.35; Cl, 8.93. Found: C, 84.90; H, 6.36; Cl, 8.95.

1-*p*-Biphenyl-1,1-diphenylbutane (8). *p*-Biphenyldiphenylmethylsodium (as prepared in the previous section) was siphoned at room temperature into 100 ml of 1-bromopropane under an atmosphere of nitrogen. The reaction mixture was worked up and recrystallized in the manner given for 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane. There was isolated some 9.3 g (41% yield) of product of mp 92.5–94°. The analytical sample after recrystallization from ethanol and twice from *n*-hexane consisted of white crystals of mp 94.7–95.3° and nmr (CCl₄) δ 7.23 (19 H, m), 2.52 (2 H, t, *J* = 6 Hz), and 0.96 (5 H, broad m).

Anal. Calcd for C₂₈H₂₆: C, 92.77; H, 7.23. Found: C, 92.87; H, 7.04.

5-*p*-Biphenyl-5,5-diphenylpentanoic Acid (6). 4-Chloro-1-*p*-biphenyl-1,1-diphenylbutane (4.35 g, 11.0 mmol), sodium cyanide (0.951 g, 19.4 mmol), and sodium iodide (1.86 g, 12.4 mmol) were placed in 300 ml of dimethyl sulfoxide and stirred with a magnetic stirrer in a stoppered flask at room temperature for 10 days.⁴³ The mixture was poured into 300 ml of water and the resin-like white product (4.0 g, 94% yield) was separated by filtration and washed with water. Attempts to purify this hard resin (crude 5-*p*-biphenyl-5,5-diphenylpentanenitrile) by recrystallization from common solvents were unsuccessful. The crude nitrile (3.15 g, 8.1 mmol) was dissolved in 80 ml of ethylene glycol containing 1.31 g of potassium hydroxide and the solution was heated at reflux for 6 hr. The usual work-up gave 3.13 g (95% yield) of crude acid, mp 97–115°. A portion (0.98 g) of this acid was recrystallized twice from glacial acetic acid and once from *n*-hexane to give 0.41 of white crystals: mp 121.5–122.5°; nmr (CCl₄) δ 11.8 (1 H, s), 7.26 (19 H, m), 2.63 (2 H, t, *J* = 7.5 Hz), 2.28 (2 H, t, *J* = 6.5

Hz), 1.46 (2 H, m).

Anal. Calcd for C₂₉H₂₆O₂: C, 85.68; H, 6.45. Found: C, 85.73; H, 6.81.

4-*p*-Biphenyl-1,1-diphenyl-1-butanol. Phenylmagnesium bromide⁴⁴ was prepared from 39.6 g (0.252 mol) of bromobenzene in 140 ml of anhydrous ether. To this solution was added dropwise with stirring 16.0 g (0.063 mol) of methyl 4-*p*-biphenylbutanoate in 50 ml of ether. The mixture was decomposed by addition of a saturated solution of ammonium chloride in water and extracted four times with ether. The ethereal extract, after drying over anhydrous MgSO₄ and removal of ether, yielded a product which after recrystallization from *n*-heptane amounted to 18.8 g (79% yield based on methyl ester) of white crystals, mp 101–103°. One recrystallization from petroleum ether (bp 30–60°) afforded white needles, mp 103.5–104.2°.

Anal. Calcd for C₂₈H₂₆O: C, 88.84; H, 6.92. Found: C, 88.78; H, 6.98.

1-Methoxy-4-*p*-biphenyl-1,1-diphenylbutane. To 6.99 g (18.5 mmol) of 4-*p*-biphenyl-1,1-diphenyl-1-butanol in 200 ml of anhydrous methanol was added 0.6 ml of concentrated sulfuric acid. A precipitate rapidly formed and after 20 min of stirring at room temperature was separated by filtration. The crystals were washed with methanol and recrystallized from anhydrous methanol to yield 6.68 g (92%) of white crystals, mp 134–136°. The analytical sample after two additional crystallizations from methanol had mp 137.2–138.0° and nmr (CCl₄) δ 7.23 (19 H, m), 2.94 (3 H, s), 2.57 (2 H, t, *J* = 7.5 Hz), 2.28 (2 H, t, *J* = 7.5 Hz), and 1.44 (2 H, quintet, *J* = 7.5 Hz).

Anal. Calcd for C₂₉H₂₈O: C, 88.72; H, 7.20. Found: C, 88.76; H, 7.42.

5-*p*-Biphenyl-2,2-diphenylpentanoic Acid (7). A solution of 6.68 g (17.0 mmol) of 1-methoxy-4-*p*-biphenyl-1,1-diphenylbutane in 35 ml of tetrahydrofuran (THF) was added dropwise over a period of 30 min to 1.52 g (0.0390 g-atom) of potassium metal stirred vigorously in 250 ml of THF at reflux temperature, according to a general procedure^{2f} for alkali metal reactions. Stirring of the deep black-red solution was continued for 1 hr at reflux temperature. The reaction solution was cooled to room temperature and then about three-fourths of the solution was forced onto crushed solid carbon dioxide and to the remainder in the reaction flask was added excess methanol. The usual work-up of the carbonated mixture gave 4.2 g of crude acid and 1.3 g of neutral material. Recrystallization of the acid from glacial acetic acid and then from *n*-hexane-acetic acid gave 2.6 g of white crystals of mp 191.4–191.8° which were identical in melting point, mixture melting point, and nmr spectrum with the acid isolated from carbonation of the reaction mixture from 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane with potassium metal in boiling THF (see subsequent description).

4-*p*-Biphenyl-1,1-diphenylbutane (9). The methanolic solution, from decomposition of 4-*p*-biphenyl-1,1-diphenylbutylpotassium with methanol in the previous preparation, yielded 1.9 g of crude hydrocarbon which was combined with the 1.3 g of neutral material obtained from carbonation of the same organopotassium compound. The combined product upon recrystallization from ethanol yielded 2.3 g of crystals of mp 78–82°. Two further recrystallizations from ethanol and one from methanol yielded white crystals of mp 81.5–82.3° and nmr (CCl₄) δ 7.18 (19 H, m), 3.88 (1 H, t, *J* = 7.5 Hz), 2.65 (2 H, t, *J* = 7.5 Hz), and 1.86 (4 H, broad m).

Anal. Calcd for C₂₈H₂₆: C, 92.76; H, 7.24. Found: C, 92.74; H, 7.14.

This hydrocarbon was identical in melting point, mixture melting point, and in spectral characteristics (ir and nmr) with the hydrocarbon isolated from methanol decomposition of the carbanion from reaction of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane with potassium in boiling THF.

General Procedure for Alkali Metal Reactions. All reactions were run in a Morton high-speed stirring apparatus according to the procedure given previously.^{2f,4} In particular all reactions with cesium and cesium alloys were conducted in a glove box under an atmosphere of nitrogen to reduce fire hazards. Also for carbonation and protonation of organoalkali products the reaction mixtures were forced under nitrogen pressure through a stainless-steel fine-mesh screen (on one end of the siphon tube) in order to remove as much unreacted alkali metal as possible.

Reactions of 4-Chloro-1-*p*-biphenyl-1,1-diphenylbutane in Tetrahydrofuran. A. With Potassium. To vigorously stirred, finely divided potassium (0.99 g, 0.0253 g-atom) in 130 ml of THF at reflux temperature was added dropwise, over a period of 10 min, 4.13 g, 0.0104 mol) of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane in 30 ml of THF. A red color instantaneously appeared upon addition of the chloride and the color rapidly deepened to black-red. The solution was allowed to cool for 8 min and then forced onto excess solid carbon dioxide. Methanol was added to the residual contents of the flask and the mixture heated at reflux for a few minutes to decompose traces of potassium. Gas-liquid partition chromatography⁴⁵ (glpc) at 254° of the methanolysis product gave the following products, listed as area per cent (relative retention time, identity): 6 (0.51), 4 (1.00, *p*-biphenyldiphenylmethane,⁴⁶ 10), 1.0 (1.54, 8), 82 (2.12, 9), 7 (2.78). The carbonation mixture was cautiously treated with water (fire hazard; use nitrogen atmosphere), concentrated *in vacuo* on a steam bath to remove THF, and extracted well with ether. The ethereal extracts were combined and extracted with 1 *N* sodium hydroxide. The ethereal layer, after drying over anhydrous MgSO₄, yielded 1.2 g of neutral material. The combined alkaline layers were strongly acidified with hydrochloric acid and extracted with ether. From the ethereal extract, after drying over anhydrous MgSO₄ and removal of ether, was isolated 3.4 g of carboxylic acid. Analysis of the neutral material by glpc at 254° gave the products, listed as area per cent (relative retention time, identity): 4 (0.51), 1.5 (1.00, 10), 4.6 (1.54, 8), 90 (2.12, 9). Analysis of a small portion of the isolated carboxylic acid by glpc⁴⁵ of its methyl ester (from reaction with diazomethane) at 254° showed the presence of only one ester at a retention time (22.9 min) shorter than that of an authentic sample of methyl 5-*p*-biphenyl-5,5-diphenylpentanoate (25.0 min). Recrystallization of a 2.0-g portion of the crude acid two times from glacial acetic acid and then from *n*-hexane gave 1.4 g of white crystals of mp 191.5–192.0° and nmr (CCl₄) δ 7.25 (19 H, m), 2.50 (4 H, m), and 1.45 (2 H, m).

Anal. Calcd for C₂₉H₂₆O₂: C, 85.68; H, 6.45. Found: C, 85.56; H, 6.71.

This carboxylic acid was identical with the sample of 5-*p*-biphenyl-2,2-diphenylpentanoic acid (7) prepared from 1-methoxy-4-*p*-biphenyl-1,1-diphenylbutane (see previous description).

In a second run under similar conditions with 1.04 g (0.00261 mol) of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane and 0.28 g (0.0071 g-atom) of potassium, the THF solution of the dark red carbanion after cooling to room temperature was decomposed by dropwise addition of 30 ml of methanol with stirring over a period of 5 min. Solvents were removed *in vacuo*, water was added to the residue, and the mixture was extracted well with ether. The ethereal extract, after drying over anhydrous MgSO₄, yielded 1.1 g of crude oil. Analysis (area per cent yields) by glpc⁴⁵ showed that the product consisted of 0.1% of 10, 1.4% of 8, and 98% of 9. Recrystallization of the crude hydrocarbon once from *n*-heptane and twice from 95% ethanol and subsequent sublimation *in vacuo* (0.3 mm, bath temperature 135°) gave 0.15 g of white solid of mp 80–81°. Further recrystallization raised the mp to 81.2–82.0°. This product was identical with the sample of 4-*p*-biphenyl-1,1-diphenylbutane (9) obtained from 1-methoxy-4-*p*-biphenyl-1,1-diphenylbutane (see previous description).

B. With Cesium. To vigorously stirred, finely divided cesium (2.21 g, 0.0166 g-atom) in 150 ml of THF at reflux temperature was added dropwise over a period of 2 min 3.00 g (7.57 mmol) of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane in 20 ml of THF. Stirring of the black-red solution was continued for 2 more min before the mixture was forced onto solid carbon dioxide. To the residual contents of the flask was added excess methanol; glpc analysis of the methanolysis product showed 2.5% of 8 and 97.5% of 9 (area per cent yields⁴⁵). The usual work-up of the carbonated mixture gave 2.6 g of solid acid and 0.40 g of neutral material. Analysis of the methyl ester of the acid by glpc showed only one peak identical in retention time with that of authentic methyl ester of 7 and different in retention time from the methyl ester of 6; similar analysis of the neutral material gave 4.4 area % of 8, 93% of 9, and 2.5% of an unknown at 0.38 times the retention time of 8 at 257°. A portion of the acid after recrystallization from glacial acetic acid and *n*-hexane consisted of white crystals of mp 190.2–191.2° which

were identical in melting point, mixture melting point, and nmr spectrum to authentic 7.

C. With Cs-K-Na Alloy. A mixture of 10.6 g (0.0795 g-atom) of cesium, 3.63 g (0.0928 g-atom) of potassium, and 0.562 g (0.0244 g-atom) of sodium in 250 ml of THF was stirred vigorously at reflux for 1 hr. After cooling down to –75° in a Dry Ice-acetone bath, the solution was stirred vigorously for 30 min and then a solution of 2.1 g (5.3 mmol) of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane in 20 ml of THF was added over a period of 30 sec. Upon addition of the first drops of chloride the solution instantly developed a deep red color. The mixture was stirred for 1 min longer until the solution suddenly developed a deep green color. About one third of the reaction mixture was quickly forced into water (hydrocarbon I) and the remainder was forced onto crushed solid carbon dioxide. Methanol was added to the carbonated mixture while Dry Ice was still present to decompose any Cs-K-Na alloy. The usual work-up gave 0.50 g of neutral product (hydrocarbon II) and 0.94 g of acids. Reaction of a portion of the acids with diazomethane and analysis of the methyl esters by glpc at 260° gave 95.4 area % of 7, no 8, and 4.6% of an unknown (likely methyl *p*-biphenyldiphenylacetate) at 0.49 times the retention time of the methyl ester of 7. One recrystallization of 0.62 g of the acid from glacial acetic acid gave 0.47 g of white crystals of mp 187–189°; further recrystallization from glacial acetic acid and then pentane gave 0.33 g of crystals of mp 190.0–191.2°, which were identical in melting point, mixture melting point, and nmr spectrum to authentic 7. Hydrocarbon I (0.61 g) on glpc analysis at 260° gave the following products, listed as area per cent (relative retention time, identity): 2 (0.82, unknown 1), 4.4 (1.00, 10), 2 (1.21, unknown 2), 15 (1.74, unknown 3), 76 (2.21, 9); hydrocarbon II similarly contained the products 0.7 (0.82, unknown 1), 17 (1.00, 10), 3 (1.21, unknown 2), 3.4 (1.74, unknown 3), and 76 (2.21, 9). Treatment of a carbon disulfide solution of hydrocarbon I with 1 g of 5% Pd-C catalyst, removal of carbon disulfide *in vacuo*, heating the residue at 125° for 20 hr under an atmosphere of nitrogen, solution in hot acetone, and filtration to remove catalyst gave a product containing greatly decreased amounts of unknowns 1, 2, and 3. Repetition of this dehydrogenation procedure with fresh catalyst for 20 hr and then again for 32 hr gave a final hydrocarbon mixture which on glpc analysis contained the following products, listed as area per cent (relative retention time, identity): 8.7 (1.00, 10), 2.8 (1.53, 8), 3.2 (1.74, unknown 3), 85 (2.21, 9). From these results it is concluded that the neutral products from this run with a large excess of Cs-K-Na alloy are complicated by a Birch-like reduction of the aromatic rings (likely the *p*-biphenyl group).

In a small scale run for nmr spectral measurements, 0.5 ml (0.73 g) of Cs-K-Na alloy, of the same composition as used previously, and 2 ml of THF were added to a small vial in a glove box filled with nitrogen. 4-Chloro-1-*p*-biphenyl-1,1-diphenylbutane (0.192 g, 0.485 mmol) was added in one portion and then the vial was tightly stoppered with a rubber septum. The solution was cooled to –75° and then the solution was stirred for 10 min with a magnetic stirrer equipped with a glass-enclosed magnet. The color of the solution turned deep red and finally black. To the solution was added through the septum with the aid of a hypodermic syringe 3 ml of mercury (to remove excess alkali metal and radical anions) over a period of 20 min with continued stirring and cooling with a Dry Ice-acetone bath. The solution was allowed to warm with stirring up to room temperature and slowly turned back to a deep red color. The amalgam was allowed to settle and some of the solution was added to a nitrogen-filled nmr tube which was then tightly sealed. Another portion of the dark red solution was decomposed with ethanol; glpc analysis⁴⁵ of the ethanolysate revealed the presence of 87 area % of rearranged hydrocarbon 9, 8% of 8, and 2% of 10. The red solution had nmr absorption (at 40°) at δ 7.17 (11.7 H, m), 6.80 (7.8 H, m), and 5.84 (2.0 H, t, *J* = 6.5 Hz). The complex multiplet centered at δ 6.80 seems to consist of a doublet at δ 6.93 (4 H, *J* = 9 Hz) overlapped by a triplet at δ 6.70 (4 H, *J* = 7.5 Hz). These nmr absorptions were measured relative to the peaks of solvent THF which were subsequently measured relative to internal TMS. By taking the hydrogens at δ 6.70 as standard of reference and on the basis that this triplet must correspond to the two para hydrogens of the diphenylmethyl portion of anion 5 while the absorption near δ 7.17 corresponds to the nine hydrogens of the *p*-biphenyl group of 5 as well as the aromatic protons of hydro-

carbons such as 8 and 10, it may be estimated from the nmr spectrum that the yield of 4-*p*-biphenyl-1,1-diphenylbutyl anion 5 is 87%, in reasonable agreement with expectations based on the glpc analysis of the products of ethanolsis.

D. With Potassium in Presence of Proton Donors. These reactions (see Table I) were run in the usual Morton high-speed stirring apparatus in 120–150 ml of THF. The THF was vigorously stirred at reflux with the potassium metal for 30–60 min (to remove any reactive proton donors from the solvent) and then a solution of the 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane and the proton source in 15–30 ml of THF was added rapidly at one time without stirring. Rapid stirring near reflux temperature was then resumed until reaction appeared to be complete (0.5–15 min). Before analysis the analytical samples were always decomposed by addition of excess methanol. Only in the case of *n*-butylamine was the reaction mixture a deep red color (as expected for the organopotassium compound 5) before addition of methanol.

For the reaction of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane (1.01 g, 2.54 mmol) in the presence of 14.2 mmol of *tert*-butyl alcohol, since 5.94 mg-atoms of potassium gave only some 17% reaction of the chloride according to glpc analysis of a 5-ml aliquot, the reaction mixture was treated with three separate additional increments of potassium and *tert*-butyl alcohol with vigorous stirring at reflux for some 5 min after each addition. Excess methanol was added to the reaction flask and the crude product was isolated in the usual fashion. Since it still contained some unreacted chloride (ca. 15%), the entire reduction procedure in THF was repeated with four incremental additions of potassium and *tert*-butyl alcohol, essentially with the quantities of reagents given in Table I for the first reduction procedure. The usual work-up gave a viscous oil which, according to glpc analysis⁴⁵ at 262°, contained the following products, listed as area per cent (relative retention time, identity): 90 (0.79, 1-*p*-cyclohexylphenyl-1,1-diphenylbutane), 3.4 (1.00, 8), 5.8 (1.09, 1-*p*-(1,4-dihydrophenyl)phenyl-1,1-diphenylbutane), 1.0 (1.37, unknown). To a carbon disulfide solution of the crude reaction product was added 1.1 g of 5% Pd-C catalyst, the solvent was removed *in vacuo*, and the mixture was heated *in vacuo* for 5 hr on a steam bath. The product was dissolved in THF and the solution was filtered to remove catalyst. Since glpc analysis indicated that dehydrogenation had started but was incomplete, the dehydrogenation was repeated with 1.4 g of 5% Pd-C catalyst at 135° for 5 hr under a nitrogen atmosphere. After removal of catalyst, analysis of the product by glpc gave a composition (retention time) of 90% 1-*p*-cyclohexylphenyl-1,1-diphenylbutane (0.79), 6.8% 8 (1.00), 2.4% 1-*p*-(1,4-dihydrophenyl)phenyl-1,1-diphenylbutane (1.09), and 0.5% of the unknown (1.37). This dehydrogenation process is interpreted to mean that the major product from the reduction with potassium was a compound not readily dehydrogenated. This result is in agreement with final assignment of the structure of 1-*p*-cyclohexylphenyl-1,1-diphenylbutane to this compound. In contrast the product of relative retention time of 1.09 is evidently dehydrogenated to 1-*p*-biphenyl-1,1-diphenylbutane (8) and, therefore, in view of the structural assignment (see below) of the major product of the reaction with potassium and in light of the structure^{7c} of the major hydrocarbon from alkali metal reduction of biphenyl, we assign this hydrocarbon the tentative structure of 1-*p*-(1,4-dihydrophenyl)phenyl-1,1-diphenylbutane. The crude reaction product was distilled *in vacuo* at a bath temperature of 130° and 0.264 g of the oily yellow product was chromatographed on a 1.5 × 15 cm column packed with alumina with elution by cyclohexane. The first fraction contained 0.237 g of colorless viscous material which after distillation at 20 μ (bath 135°) gave 0.12 g of white crystals. After recrystallization from 95% ethanol the product had mp 100.6–102.0°: λ_{max} (EtOH) 260 nm (ϵ 952); nmr (CCl₄) δ 7.10 (14.0 H, m), 2.48 (2.1 H, t, J = 7 Hz), 2.2 (0.9 H, broad m), 2.0–1.0 (12.2 H, complex m), 0.91 (2.9 H, ca. t) (ratio of aromatic to all other hydrogens, 14.0:18.1); mass spectrum m/e (rel intensity, assignment), 368 (2.5, C₂₈H₃₂⁺), 325 (100, C₂₅H₂₅⁺), 167 (24, C₁₃H₁₁⁺), 165 (30, C₁₃H₉⁺), 43 (36, C₃H₇⁺), 41 (23, C₃H₅⁺). The structure of 1-*p*-cyclohexylphenyl-1,1-diphenylbutane is accordingly assigned this compound.

Anal. Calcd for C₂₈H₃₂: C, 91.24; H, 8.76. Found: C, 91.02; H, 8.99.

Reactions of 4-Chloro-1-*p*-biphenyl-1,1-diphenylbutane in Dioxane. A. With Sodium. Purified dioxane (150 ml) was stirred vigorously for 1 hour at reflux with 0.442 g (19.2 mg-atoms) of sodium

and then 5% of a solution of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane (3.0 g, 7.6 mmol) in 30 ml of dioxane was added. Since no appreciable color change was observed after 20 min of vigorous stirring, 0.23 g (1.6 mmol) of methyl iodide and 0.21 g (0.72 mmol) of 2-chloro-1,1,1-triphenylethane^{2a} in dioxane were added. The reaction mixture developed the violet color of Wurtz sodium halide but no red color attributable to a carbanion was observed throughout the reaction. The remainder of the chloride solution was added dropwise over a period of 20 min, the mixture was stirred vigorously at reflux for an additional 30 min, and then the reaction mixture was forced onto solid carbon dioxide. The usual work-up gave 3.3 g of neutral material but no carboxylic acid. Analysis⁴⁵ of the neutral material at 254° by glpc revealed the presence of 96 area % of 8, no 9, and 4% unreacted chloride.

The first run was repeated but with stirring with 2.77 g (0.120 g-atom) of sodium for 1 hr at reflux before addition of 3.34 g (0.0361 mol) of *n*-butyl chloride in 20 ml of dioxane over a period of 15 min. Addition of 1.83 g (0.00461 mol) of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane in 15 ml of dioxane, and completion of the reaction as previously, gave 1.80 g of neutral material and no carboxylic acids. Analysis by glpc of this neutral material and the product from treatment of the residual contents of the reaction flask with ethanol gave the same results (see Table I). Fractional crystallization of the neutral material from *n*-heptane gave 1.1 g of crystals of mp 88–93°; two more recrystallizations from heptane and one recrystallization from ethanol gave 0.24 g of crystals, mp 94.2–95.0°, which were identical in melting point, mixture melting point, and nmr spectrum with the sample of 8 prepared from *p*-biphenyldiphenylmethylsodium and 1-bromopropane.

In a final run, 400 ml of purified dioxane was stirred for 1 hr at reflux temperature with 3 g of potassium under a nitrogen atmosphere in the usual Morton high-speed stirring apparatus. This further purified dioxane (250 ml) was then directly distilled into a second apparatus containing 2.28 g (0.099 g-atom) of sodium. The mixture was stirred vigorously at reflux temperature for 1 hr and then 3.29 g (0.0356 mol) of *n*-butyl chloride in 20 ml of dioxane (further purified as described above from potassium) was added dropwise over a period of 15 min. Next 2.10 g (0.0053 mol) of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane in 20 ml of dioxane (further purified as described from potassium) was added over a period of 15 min with stirring at reflux continued for an additional hour before addition of a 10-ml aliquot to excess methanol and carbonation of the remainder. The usual work-up gave 1.8 g of neutral material from carbonation and negligible acids (~0.03 g), none of which were volatile as methyl esters under usual glpc conditions. The neutral materials from carbonation and methanolysis were identical within experimental error according to analysis by glpc (see Table I).

B. With Potassium. Purified dioxane (150 ml) was vigorously stirred with potassium (4.79 g, 0.123 g-atom) at reflux temperature for 30 min. A solution of 2.87 g (0.031 mol) of *n*-butyl chloride in 20 ml of dioxane was added dropwise over a period of 15 min. Next a solution of 2.02 g (0.00509 mol) of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane in 20 ml of dioxane was added dropwise to the vigorously stirred solution over a period of 20 min. About half way through this addition a reddish brown color appeared in the solution and the color deepened to black-red at the end of the addition. The reaction mixture was stirred an additional 1 min before cooling to room temperature and carbonation. The usual work-up gave 1.45 g of neutral product and 0.57 g of crude acids. Analysis⁴⁵ of the neutral product by glpc at 300° gave the following products listed as area per cent yield (relative retention time, identity): 1 (0.45), 3 (0.52), 3 (0.71), 2 (0.87), 1.6 (1.00, 10), 77 (1.94, 9), and 11 (2.90), with no hydrocarbon 8 found. A quantitative glpc analysis revealed that the absolute yield of 9 was, in fact, 75% by weight of the crude neutral product. The neutral product obtained from ethanolsis of a small portion of the original reaction mixture had the same area ratio of the two major components as in the product from carbonation. Analysis of the acidic products, determined as methyl esters by glpc at 300°, gave the products, listed as previously, 5 (0.73), 6 (0.92), 8 (1.00, 7), 39 (1.29), 10 (1.63), as well as five compounds of shorter retention time than those listed. Since the absolute yield of 7 was only 8.7 mg or 1.5% by weight of the crude acids, the crude acid obviously consisted of a complex mixture of cleavage products as well as materials of higher molecular weight than 7.

C. With Cesium. Purified dioxane (250 ml per run) was distilled from potassium. In the run at 40° upon addition of cesium metal to the dioxane, gas evolution was observed and after stirring for 30 sec the solution was quite cloudy (much cleavage of dioxane by cesium). Upon addition of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane (all in one portion in 20 ml of dioxane) the solution developed an instantaneous red color which rapidly disappeared. The solution was stirred for 30 sec before carbonation and treatment of the residual contents of the flask with ethanol. The usual work-up gave only neutral materials and no carboxylic acids; the products of carbonation were identical with those of ethanolysis (see Table I). The nmr spectrum of the crude product was that expected for hydrocarbon 9 with minor impurities.

A second run with 0.974 g (2.46 mmol) of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane was initiated at a lower temperature in order to decrease the amount of reaction of cesium (5.1 g) with dioxane; however, after addition of the chloride the temperature rose to 37° within 1 min and developed a brown-pink color. After stirring for 5 min, a 5-ml aliquot was decomposed with methanol (see Table I). An additional 5.2 g (39 mg-atoms) of cesium was added and the solution was stirred vigorously for 10 min (deep red color) before carbonation. The usual work-up gave 0.62 g of neutral material and 0.27 g of acids. A quantitative glpc analysis of the methyl esters of the acid fraction gave only a 0.13% yield (based on starting chloride) of 7 and comparably small amounts of four unknown acids which had volatile methyl esters at 264°. Analysis of the neutral fraction by glpc under the same conditions gave the following products, listed as area per cent yield (relative retention time, identity): 3 (1.00, A), 32 (1.3, B), 1.2 (3.0, C), 54 (4.3, D), 9.7 (5.3, 9). These products after separation by glpc were analyzed by mass spectrometry. Compound A had mass spectrum *m/e* (rel intensity, assignment) 250 (23, C₁₉H₂₂⁺), 249 (100, C₁₉H₂₁⁺), 167 (22, C₁₃H₁₁⁺), 165 (25, C₁₃H₉⁺), 91 (44, C₇H₇⁺), 83 (8, C₆H₁₁⁺), and 81 (8, C₆H₉⁺); in accord with this spectrum and other general evidence this compound is assigned the tentative structure of *p*-cyclohexyldiphenylmethane. Compound B (12% absolute yield) had mass spectrum 292 (38, C₂₂H₂₈⁺), 210 (18, C₁₆H₁₈⁺), 201 (3, C₁₅H₂₁⁺), 173 (31, C₁₃H₁₇⁺), 159 (40, C₁₂H₁₅⁺), 133 (6, C₁₀H₁₃⁺), 131 (56, C₁₀H₁₁⁺), 117 (41, C₉H₉⁺), and 91 (100, C₇H₇⁺); the exact mass was 292.2204 (calcd for C₂₂H₂₈: 292.2191); hence compound B is assigned the tentative structure of 4-*p*-cyclohexylphenyl-1-phenylbutane. Compound C (0.3% absolute yield) had a mass spectrum identical with that of 1-*p*-cyclohexylphenyl-1,1-diphenylbutane isolated from the reaction of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane with potassium in THF containing *tert*-butyl alcohol. Compound D (16% absolute yield) had mass spectrum, 368 (36, C₂₈H₃₂⁺), 201 (3, C₁₅H₂₁⁺), 193 (16, C₁₅H₁₃⁺), 186 (14, C₁₄H₁₈⁺), 180 (19, C₁₄H₁₂⁺), 173 (9, C₁₃H₁₇⁺), 171 (22, C₁₃H₁₅⁺), 168 (51, C₁₃H₁₂⁺), 167 (100, C₁₃H₁₁⁺), 165 (28, C₁₃H₉⁺), 117 (20, C₉H₉⁺), and 91 (42, C₇H₇⁺); the exact mass was 368.2506 (calcd for C₂₈H₃₂: 368.2504). Compound D is accordingly assigned the tentative structure of 4-*p*-cyclohexylphenyl-1,1-diphenylbutane.

Reactions of 4-Chloro-1-*p*-biphenyl-1,1-diphenylbutane. A. With Lithium. In the usual apparatus was placed 250 ml of THF and 1.87 g (0.269 g-atom) of lithium wire cut into small pieces. Methyl iodide (0.1 ml) was added with vigorous stirring at room temperature and then the reaction mixture was cooled to -70° before dropwise addition of a solution of 6.76 g (0.0170 mol) of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane in 20 ml of THF over a period of 30 min. After stirring for 2 more hr the deep red solution was forced onto solid carbon dioxide. The usual work-up gave 2.0 g of neutral material (glpc, 45 area per cent yields: 2% 10, 77% 8, 10% 9, 8% starting RCl) and 4.8 g of crude acids (glpc analysis at 262°, area per cent yields (relative retention time, identity): 21 (1.00, 7), 79 (1.08, 6)).

In a second run which was conducted similarly at -70° with 1.86 g of lithium and 7.27 g (0.0184 mol) of chloride, the deep red solution after stirring for 2 hours following completion of the addition of chloride turned almost black over a period of 5 min. The reaction solution was then forced through a fine stainless steel screen on the end of a siphon tube (to remove excess lithium) into a nitrogen-filled flask for storage at 0° (ice bath). Hydrolysis of the residual reaction mixture in the flask gave a product which on glpc analysis at 262° gave area per cent yields (relative retention time, identity) of 1 (1.00, 10), 3 (1.21, 8 + 6 H), 66 (1.49, 8), 21 (2.08,

9), 4 (2.44), and 5 (2.71, unreacted chloride = RCl). The organolithium reagent after storage at 0° for 4 hr was carbonated and the flask residue was hydrolyzed. The latter hydrolysate on glpc analysis gave products, listed as previously, 1 (1.00, 10), 54 (1.49, 8), 25 (2.08, 9), 8 (2.44), 7 (2.71, RCl), 5 (3.05). The usual work-up of the carbonated mixture gave 1.2 g of crude acids and 4.3 g of neutral product. The acids on glpc as methyl esters at 262° contained products, listed as previously, 83 (1.00, 7) and 17 (1.08, 6), while the neutral product similarly contained 0.5 (1.00, 10), 61 (1.49, 8), 14 (2.08, 9), 9.5 (2.44), 9.5 (2.71, RCl), and 6 (3.05).

A repetition of the last run yielded at -75° an initial organolithium reagent which upon carbonation of an aliquot gave a 22:78 ratio by weight of neutral material to acids, the acids consisting of a 78:22 ratio of 6 to 7. Hydrolysis of another aliquot of the organolithium reagent gave a mixture of hydrocarbons which contained 22 area % of rearranged hydrocarbon 9. After storage of the organolithium reagent for 8 hr at -11°, carbonation gave a 93:7 ratio by weight of neutral material to acids. The neutral material contained 65 and 19 area % 8 and 9, respectively, while the acids consisted of a 26:74 ratio of 6 to 7. Hydrolysis of an aliquot of the lithium reagent which had been stored at -11° gave a mixture of hydrocarbons containing 24 area % of 9 and 50% of 8.

B. With Lithium Followed by Potassium *tert*-Butoxide. Two of the usual Morton high-speed stirring apparatuses were set up side by side such that the contents of one flask could be forced under pressure of nitrogen through a tube into the second flask. To one flask were added 300 ml of THF, 9.53 g (0.244 g-atom) of potassium, and then, after the solution came to reflux temperature, 8.9 g (0.12 mol) of *tert*-butyl alcohol dropwise over a period of 30 min with vigorous stirring under an atmosphere of nitrogen. The solution was kept at reflux with vigorous stirring for an additional 90 min before cooling, finally to -75°. To the other flask were added 250 ml of THF, 1.54 g (0.223 g-atom) of lithium, and 0.10 ml (1.6 mmol) of methyl iodide; the mixture was stirred vigorously for 10 min at room temperature before cooling to -75°. A solution of 0.943 g (0.0102 mol) of *n*-butyl chloride in 10 ml of THF was added with stirring to the cold solution over a period of 20 min. This was followed immediately by the addition of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane (1.00 g, 2.53 mmol) in 15 ml of THF over a period of 20 min. When after 90 min of additional stirring at -75° the pink solution developed a black coloration, stirring was stopped and a 5-ml aliquot was decomposed with methanol (hydrocarbon A). To the remainder of the reaction mixture at -75° was added ca. 150 ml of the cold potassium *tert*-butoxide solution (freed from the coagulated potassium metal by passage through a fine-meshed stainless-steel screen on the end of the transfer tube). The solution instantly developed a dark pink color. The mixture was stirred for 0.5 min and then was kept at -75° for 10-min before methanolysis of a 5-ml aliquot (hydrocarbon B) and carbonation of the remainder. The carbonated mixture was worked up in the manner previously given⁴ for carbonated organolithium compounds to give 0.34 g of crude neutral material (hydrocarbon C) and 0.67 g of acid. Analysis by glpc⁴⁵ at 266° indicated that hydrocarbon A had 52 area % of 8 and 46% of 9 while hydrocarbon B had 24% of 8 and 75% of 9 as well as 1-2% each of an unknown at 2.12 times the retention time of 8. Quantitative glpc analysis of hydrocarbon C indicated the presence of 0.13 g (14%) of 8, 0.07 g (8%) of 9, and 7 area % of the same unknown hydrocarbon. Analysis of the acid fraction, by quantitative glpc as methyl esters at 258°, indicated the presence of 0.61 g (58% yield based on starting chloride) of 7 and no 6, and the remainder (~0.06 g) consisted of approximately equal amounts of four unknowns at 0.65, 0.72, 1.19, and 1.62 times the retention time of 7. A repetition of this run but with reaction times of 1, 2, and 3 hr at -75° after addition of potassium *tert*-butoxide gave on methanolysis three identical mixtures of hydrocarbons, essentially of the composition of hydrocarbon B, as expected if rearrangement is complete in less than 10 min at -75°.

In another run 0.976 g (0.141 g-atom) of lithium in 250 ml of THF was similarly treated with 0.03 ml of methyl iodide at room temperature and then 0.44 g (4.8 mmol) of *n*-butyl chloride and 3.00 g (7.58 mmole) of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane at -75°. A 10-ml aliquot was decomposed with methanol (hydrocarbon A) and to the remainder was added ca. 150 ml of potassium *tert*-butoxide (0.044 mol) in THF at -75°. The mixture was stirred for 0.5 min and allowed to stand for 5 min at -75° be-

fore methanolysis of a 10-ml aliquot (hydrocarbon B) and carbonation of the remainder. From the carbonation there was isolated 1.4 g of neutral material (hydrocarbon C) and 1.58 g of acid. The usual glpc analysis gave for hydrocarbon A 61 area % of 8 and 36% of 9 and for hydrocarbon B 29 area % of 8 and 63% of 9. Quantitative glpc analysis of hydrocarbon C gave 0.64 g (24% yield) of 8, 0.19 g (7% yield) of 9, and 0.02 g (0.7%) of 1-*p*-(1,4-dihydroxyphenyl)phenyl-1,1-diphenylbutane; similar analysis of the acid gave 1.51 g (49% yield) of 7, no 6, and traces of two unknown acids of 0.45 and 0.49 times the retention time of 7. The nmr spectrum of the acid was essentially the same as that of an authentic sample of 5-*p*-biphenyl-2,2-diphenylpentanoic acid.

C. With Lithium Biphenylide. To 300 ml of THF was added 0.701 g (0.101 g-atom) of lithium and 1.0 ml (16 mmol) of methyl iodide. The solution was stirred vigorously at room temperature for 10 min and then 7.7 g (0.050 mol) of biphenyl was added. Upon stirring the solution rapidly developed a deep blue color and was thereupon cooled to -75° with stirring continued for 4 hr. The cold solution was then siphoned through a fine stainless steel screen (to remove excess lithium metal) into an adjacent Morton flask equipped with a high speed stirrer. Double Gilman⁴⁷ titration indicated that the solution was 0.050 *M* in lithium biphenylide or that the remaining solution contained some 12 mmol of reagent. To the well-stirred solution at -75° was added dropwise first 0.219 g (2.37 mmol) of *n*-butyl chloride in 10 ml of THF (to scavenge any impurities present) and then, over a period of 5 min, 0.956 g (2.41 mmol) of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane in 20 ml of THF. Upon addition of the latter chloride, the solution gradually changed to a green-blue color and, 1 min after completion of the addition, to a pink color. The reaction mixture was carbonated and the small residue in the flask decomposed with methanol. The methanolysis product upon glpc analysis contained area per cent yields as follows: 90% of 8, 8.1% of 9, and 2% of unreacted chloride. The carbonated product afforded 0.84 g of crude acids and, according to quantitative glpc analysis, 0.05 g of volatile neutral products in the recovered biphenyl. The acids on quantitative glpc analysis (as methyl esters) contained 63% yield (based on starting chloride) of 6 and 5.1% of 7 while the neutral product similarly consisted of 3% yield of 8, 0.13% of 9, 0.08% of 10, and 2% of unreacted chloride.

In a similar reaction of 1050 ml of 0.016 *M* lithium biphenylide with 2.6 mmol of *n*-butyl chloride and then 2.5 mmol of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane, the product of methanolysis contained by glpc analysis area per cent yields: 4% 10, 85% 8, and 12% 9. The product of carbonation, however, contained only some 8% yield of volatile acids, presumably because of experimental difficulties in working with such a dilute solution of organolithium compounds.

In a similar reaction of 240 ml of 0.26 *M* lithium biphenylide with 2.4 mmol of *n*-butyl chloride and then 2.5 mmol of 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane, the product of methanolysis contained, according to analysis by glpc, the area per cent yields: 6% 10, 92% 8, 2.0% 9. The product of carbonation according to quantitative glpc analysis (yields based upon the starting chloride) contained, in the neutral product, 13% of 10, 26% of 8, and 1.1% of 9 and, in the acidic product, 39% of 6 and 1.0% of 7.

Reaction of Neophyl Chloride with Lithium Biphenylide. To 300 ml of THF was added 1.23 g (0.177 g-atom) of finely cut lithium and 1.0 ml (16 mmol) of methyl iodide. The solution was stirred vigorously for 5 min at room temperature and then 26.3 g (0.171 mol) of biphenyl was added. After 5 min of additional stirring the deep blue solution was cooled to -75° with vigorous stirring continued for 4 hr. A solution of 1-chloro-2-methyl-2-phenylpropane (5.61 g, 33.3 mmol) in 20 ml of THF was added dropwise to the well-stirred mixture over a period of 80 min at -75° . After 15 more min of stirring the green mixture was forced onto crushed solid carbon dioxide. The usual work-up gave 4.5 g of crude acid. Analysis of the neutral and acidic product by glpc on a 6 ft \times 0.25 in. column packed with 10% Apiezon L on 60-80 mesh Chromosorb G (acid washed and treated with dimethyldichlorosilane) at 148° gave absolute yields of 0.21 g (4.5%) of *tert*-butylbenzene, 0.93 g (17% recovery) of unreacted chloride, 0.055 g (0.9%) of 2,2-dimethyl-3-phenylpropanoic acid, and 4.5 g (76%) of 3-methyl-3-phenylbutanoic acid.

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Carbanions. XVI. Reactions of 4-Chloro-1-*p*-biphenylbutane with Alkali Metals. Formation of a Spiro Anion¹

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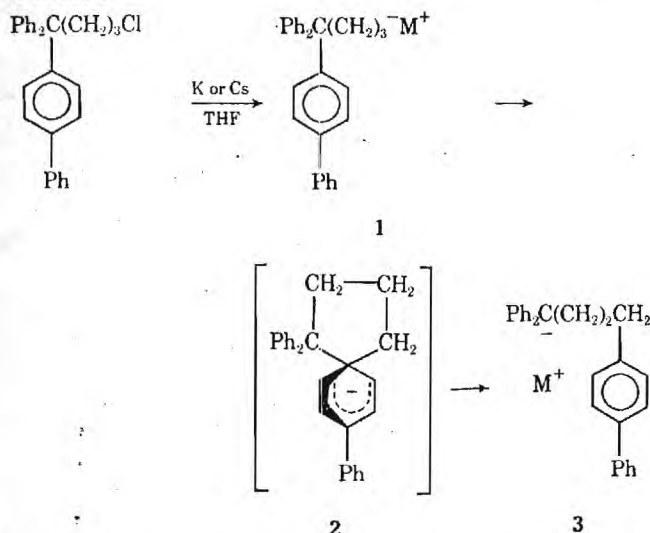
*Contribution from the School of Chemistry, Georgia Institute of Technology,
Atlanta, Georgia 30332. Received December 9, 1974*

Abstract: 4-Chloro-1-*p*-biphenylbutane reacts with lithium in THF at -70° to give a mixture of 4-*p*-biphenylbutyllithium and 8-phenylspiro[4.5]-6,8-decadienyllithium (7). With potassium, cesium, and Cs-K-Na alloy chiefly the spiro anion (7) and a little 1-*p*-biphenylbutyl anion (6) are formed. Experiments with sodium and potassium, in which dioxane or tertiary alcohols were used as a proton source to "trap" intermediate anions, indicate that 4-*p*-biphenylbutyl anion (5, M = K or Cs) is a precursor of 7. From labeling experiments no evidence was found for the spiro anion 7 reverting back to the open anion 5. The 4,4-diphenyl groups of 4-*p*-biphenyl-4,4-diphenylbutyl anion facilitate both spiro cyclization and ring opening.

In a previous work,² it was shown that 4-chloro-1-*p*-biphenyl-1,1-diphenylbutane reacts with potassium or cesium in tetrahydrofuran (THF) to give 4-*p*-biphenyl-1,1-diphenylbutyl anion. Evidence was presented that this reaction proceeds according to Scheme I. Attempts, however, to detect the intermediate spiro anion 2 were unsuccessful

even from a reaction of Cs-K-Na with the chloride at -75° for some 2 min, whereupon only the rearranged anion 3 was present, according to the products of carbonation or protonation. Since the anion 3 is stabilized by the two phenyl groups on carbon-1 which serve to delocalize the negative charge, it was thought possible that if these phenyls were

Scheme I

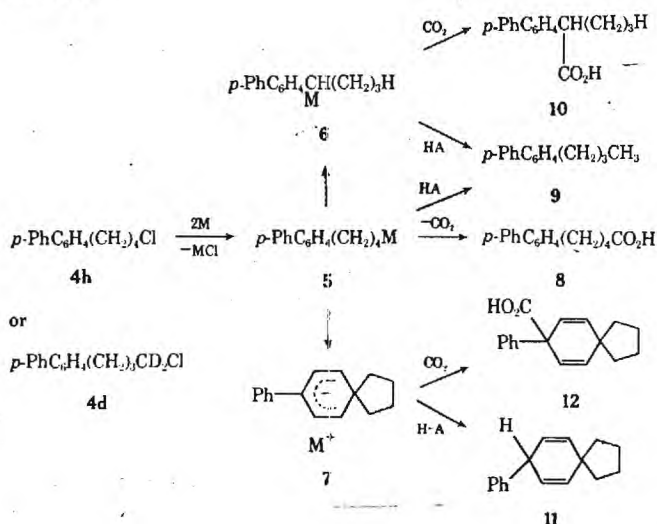


lacking in the spiro anion 2, the resulting spiro anion might be stable. Accordingly a study of the reactions of 4-chloro-1-p-biphenylbutane (4) with alkali metals was undertaken.

Results

4-Chloro-1-p-biphenylbutane (4h) was allowed to react with alkali metals and the products of reaction were identified after protonation or carbonation to give the corresponding hydrocarbons or carboxylic acids as shown in Scheme II. From reaction of 4h with lithium in THF at

Scheme II



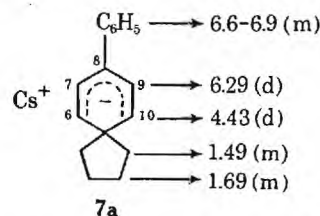
−70°, an organolithium reagent was obtained which upon carbonation gave a good yield of carboxylic acids which proved to be a mixture of 5-p-biphenylpentanoic acid (8) and 8-phenylspiro[4.5]deca-6,9-diene-8-carboxylic acid (12) in a molar ratio of 63 to 37, respectively. Repetition of this run with 4-p-biphenyl-1-chlorobutane-1,1-d₂ (4d) gave a similar ratio of 8 to 12 with product 8 consisting entirely of 5-p-biphenylpentanoic-2,2-d₂ acid. This result indicates that the spiro anion 7 (Scheme II, M⁺ = Li⁺), which is doubtlessly the precursor of 12, does not undergo ring opening to generate the organolithium compound 5 to any appreciable extent at −70°. In an effort to see if 5 will cyclize to 7, the organolithium reagent prepared at −70° was held at −5° for 3 hr; however, because carbonation gave only a low yield of acid (essentially entirely 12) and

much hydrocarbon and polymer, the result was indecisive. Since in other carbanion rearrangements organolithium reagents have been found to be much less reactive than potassium and cesium compounds,^{2,3} we directed our attention to study of the latter.

Reaction of the chloride 4h with finely divided potassium in THF at 65° for about 10 min before cooling and carbonation gave 22% yield of spiro acid 12, 6% of 2-p-biphenylpentanoic acid (10), and 9% of 1-p-biphenylbutane (9) with the remainder primarily hydrocarbons and acids which were nonvolatile under conditions of gas chromatographic analysis. Repetition of this run with the labeled chloride 4d but with decomposition by ice-water gave a 2:1 ratio of hydrocarbons 9 and 8-phenylspiro[4.5]deca-6,9-diene (11). Hydrocarbon 9 consisted of >99% of 1-p-biphenylbutane-4,4-d₂; hence also under the present conditions no appreciable quantity of 9 is formed from the spiro anion 7.

Reaction of the chloride 4h with cesium in THF at 65° gave upon carbonation about the same low yield of spiro acid 12 and α metallation product 10 as with potassium; however, when the temperature of reaction was lowered to 35°, the yields of 12 and 10 rose to 59 and 10%, respectively. With Cs-K-Na alloy⁴ in THF at −70°, the yield increased to at least 76% of 12 along with 4% of 10. Attempts to characterize the spiro anion 7 by protonation rather than carbonation gave low yields (ca. 6%) of 8-phenylspiro[4.5]deca-6,9-diene (11) under all the conditions tested; the chief material obtained from hydrolysis was nonvolatile under the conditions of GLC analysis and evidently resulted from oligomerization processes involving the diene 11 or its conjugated isomer.

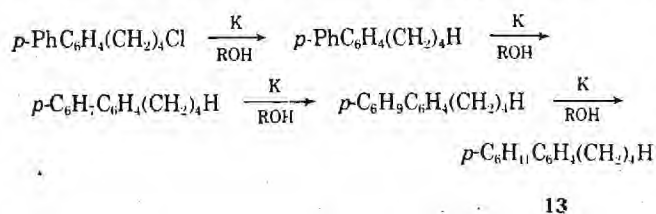
The spiro anion 7 from reaction of the chloride 4h with Cs-K-Na alloy⁵ at −70° was further characterized by its proton NMR spectrum at 40° in tetrahydrofuran-d₈ as summarized in units of δ in 7a. This carbanion has the



NMR spectrum expected for structure 7 by analogy with the spectrum⁶ of 6,6-dimethylcyclohexadienyllithium in THF-hexane (δ 3.4 and 5.9 vs. δ 4.43 and 6.29, respectively, in 7a) if it is considered that some of the negative charge of the spiro anion should reside on the phenyl substituent. The corresponding lithium compound was prepared⁷ by reaction of *n*-butyllithium upon hydrocarbon 11 in THF-heptane and showed a similar spectrum except that the hydrogens of the cyclohexadienyl moiety absorbed at δ 4.24 and 6.48 rather than as shown in 7a. This spectral difference might be attributed⁸ to the lithium compound existing in large part as a loose (solvent separated) ion pair while the cesium compound likely exists more as a tight (contact) ion pair at 40°. In the tight ion pair the shielding of hydrogens at C-6 and C-10 appears to be decreased relative to that in the loose ion pair as has been observed previously,⁸ however, the shielding at C-7 and C-9 appears to be proportionately increased such that the tight ion pair appears to have a somewhat more even distribution of charge than the loose ion pair.

In order to attempt to trap intermediates in the reaction of 4-chloro-1-p-biphenylbutane (4h) with alkali metals, the reaction was run in the presence of various proton donors. Addition of a THF solution of 4h containing excess *tert*-butyl alcohol to a large excess of potassium in THF at

reflux temperature gave a 90% yield of 1-(*p*-cyclohexylphenyl)butane (**13**) and 2% of 1-*p*-biphenylbutane (**9**). Repetition of this experiment with 2 g-atoms of potassium per mol of **4h** gave only 17% of **13** while the yield of **9** rose to 11% and 62% of the chloride remained unreacted. When the first experiment was repeated with **4d**, the product **13** proved to be labeled predominantly as *p*-(C₆H₁₁)-C₆H₄CH₂CH₂CH₂CD₂H according to its NMR spectrum. Finally the reaction was repeated with 3 g-atoms of potassium per mole of **4h** and with 3.4 mol of 3-ethyl-3-pentanol in place of excess *tert*-butyl alcohol; there resulted 27% of **13**, 6% of spiro hydrocarbon **11**, 9% of 1-*p*-biphenylbutane (**9**), and about 25 and 9%, respectively, of dihydro and tetrahydro derivatives of **9**. These results show that in the presence of excess potassium and proton donor, the reaction can be interrupted in high yield at a stage prior to appreciable cyclization. Furthermore, as the quantity of potassium and the activity of the protonating agent are decreased, a little spiro cyclization occurs but the products are predominantly 1-*p*-biphenylbutane and its products of reduction. The main reduction sequence, therefore, appears to be



This reaction constitutes another example of a general method² for the reduction of a 4-alkylbiphenyl to a 4-cyclohexyl-1-alkylbenzene.

Since dioxane has been found to protonate carbanions readily^{2,9} but without the complications of appreciable direct reaction of dioxane with sodium or potassium or of Birch-like reductions of the *p*-biphenyl group with these metals, reactions of 4-chloro-1-*p*-biphenylbutane were studied in this solvent. The chief product with sodium after carbonation was 1-*p*-biphenylbutane; this product from the labeled chloride **4d** was >98% 1-*p*-biphenylbutane-4,4-*d*₂ according to analysis by NMR and mass spectrometry. With potassium after carbonation the product was 18% of spiro hydrocarbon **11**, 60% of **9**, 1.7% of spiro acid **12**, and 0.3% of **10**; compound **9** from **4d** was >89% 1-*p*-biphenylbutane-4,4-*d*₂. In dioxane spiro cyclization obviously occurs more readily with potassium than with sodium.

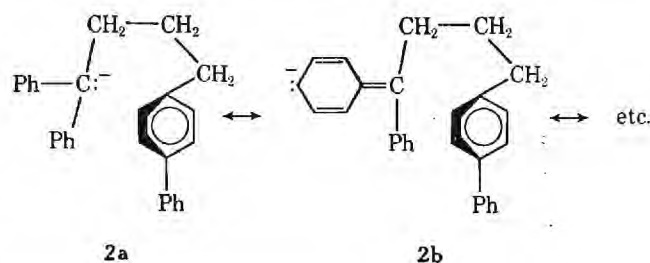
Discussion

The experiments in which 4-chloro-1-*p*-biphenylbutane was allowed to react with potassium in THF in the presence of *tert*-butyl alcohol or 3-ethyl-3-pentanol gave 1-*p*-biphenylbutane (**9**) or products derived therefrom by further reduction. We believe that this result indicates that the chloride reacts with potassium to give the corresponding organopotassium compound **5** which is protonated by the alcohol to give **9** (see Scheme II). The alternative possibility that *tert*-butyl alcohol donates a hydrogen atom to an intermediate free radical derived from the chloride is most unlikely on the following basis. Alkyl radicals are very similar to hydrogen atoms in their rate of abstraction of hydrogen atoms from organic compounds and since hydrogen atoms abstract hydrogen from THF more than 150 times more readily than from *tert*-butyl alcohol,¹⁰ the intermediate trapped by addition of *tert*-butyl alcohol in the present experiments must be the organopotassium compound **5** rather than the corresponding free radical. Since the rearrangement is blocked by *tert*-butyl alcohol and other proton donors, the forma-

tion of **5** precedes cyclization and likely cyclization takes place by way of **5**.

While the organopotassium and -cesium compounds **5** cyclized rapidly under the conditions of the present experiments, the corresponding organolithium compound was comparatively stable at -70° as expected by analogy with other organolithium compounds which are capable of undergoing rearrangement.^{2,3,11} Hence the fact that reaction of the chloride **4h** with lithium metal at -70° gave a mixture of organolithium compound **5** along with the spiro anion **7** is taken to mean that **7** is formed not from **5** but from some precursor of **5**. Similar observations have been made in related cases.^{2,12}

An interesting observation in the present work is the slow rate of rearrangement (*k_R*) of 4-*p*-biphenylbutylsodium (**5**) to **7** compared with the rate of protonation (*k_H*) of this organosodium compound by dioxane at 101°; the relative rate *k_R*/*k_H* is less than 0.02. In contrast for 4-*p*-biphenylbutylpotassium under the same conditions the value of *k_R*/*k_H* is 0.33. While these relative rate ratios doubtlessly reflect the effect of the alkali metal cation on both the rate of protonation and the rate of spiro cyclization, we suggest that the larger effect is on the latter rate; large alkali metal cations evidently favor spiro-cyclic addition to aryl groups. Since such addition is postulated to be a key step in 1,4 rearrangement of the *p*-biphenyl group (see Scheme I), it is agreeable to note that large cations have also been found to favor 1,4 rearrangement. In particular the ratio of the rate of 1,4 rearrangement of the *p*-biphenyl group to the rate of protonation by solvent (*k_R*/*k_H*) for 4-*p*-biphenyl-4,5-diphenylbutyl alkali compounds in dioxane at 101° is 0.08 for sodium and >80 for potassium.² While the trend in the ratios on going from sodium to potassium is similar for the two series, the ratios for a given alkali metal cation are larger for the 4-*p*-biphenyl-4,4-diphenylbutyl alkali compounds than for the 4-*p*-biphenylbutyl alkali compounds, e.g., >240-fold larger with K⁺. This result implies that the additional two phenyl groups in 4-*p*-biphenyl-4,4-diphenylbutyl as opposed to 4-*p*-biphenylbutyl alkali compounds accelerate the spiro cyclization reaction relative to protonation by the solvent. This acceleration can be understood in terms of delocalization of the negative charge in **2** (or the transition state leading to **2**) by the phenyl groups as described by contributions from canonical structures such as **2a** and **2b** to the structure of **2**. What the present work

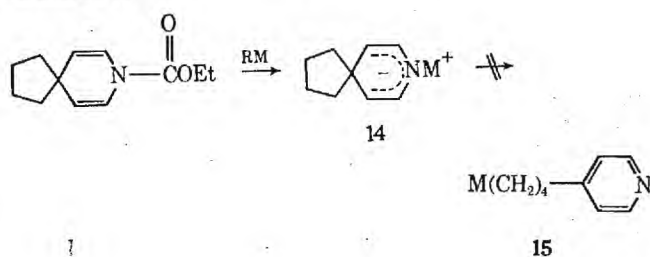


leaves unresolved is whether **2** is best described as an intermediate or a transition state from **1** to **3**. In this regard it is of interest to note that while the conversion of 4-*p*-biphenylbutyl alkali compounds **5** to the spiro compound **7** is now well documented, no evidence was obtained for reversion of **7** back to **5**. Evidently the two phenyl groups on C-1 of structure **2** greatly facilitate ring opening as well as ring closure.

In the present work some 5 to 10% of an anion **6**, formed by an apparent 1,4 proton migration (see Scheme II), was observed during reactions of chloride **4h** with potassium and cesium. While an intramolecular proton migration appears

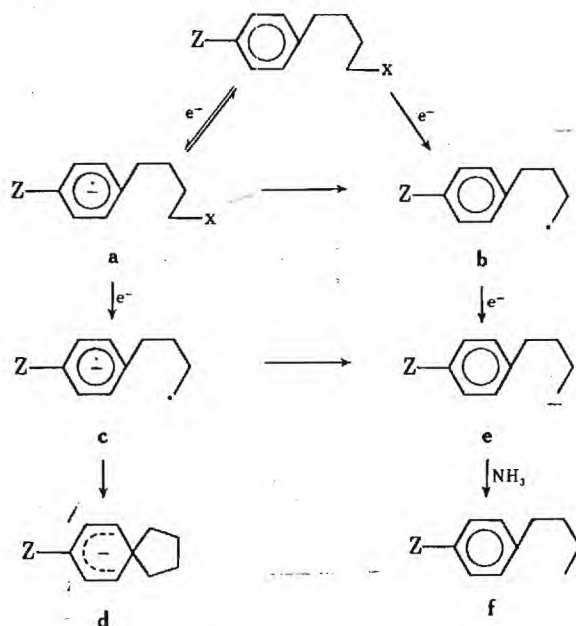
to be an attractive route to **6**, the true mechanism of formation of **6** remains to be established.¹³

Fraenkel, Ho, Liang, and Yu¹⁴ have recently described the synthesis of the spiro anion **14**. This stable spiro anion gave no evidence for ring opening to **15**; evidently the hetero nitrogen atom stabilizes **14** much as the phenyl substituent stabilizes **7**.



Since our work was begun¹ Julia and Malassiné¹⁵ have reported a similar cyclization in the reactions of *p*-(4-halo-butyl)benzoic acids with alkali metals in liquid ammonia. They found that the amount of spiro product decreased as halogen varied along the series $\text{Cl} > \text{Br} > \text{I}$ and suggested the mechanism shown in Scheme III ($\text{Z} = \text{CO}_2^-$). This mechanism makes a subtle distinction between electronic isomers, the carbanion **e** (which alone is protonated to **f**) and the diradical anion **c** (which alone cyclizes to **d**). Our results can be made to accord with a modification of Scheme III ($\text{Z} = \text{Ph}$) if we postulate that for the 4-*p*-bi-

Scheme III



phenylbutyl system the cyclization $\text{c} \rightarrow \text{d}$ occurs more slowly than the collapse of the diradical anion $\text{c} \rightarrow \text{e}$ (this might be true because in the biphenyl system the charge on the radical anion is more highly delocalized than in the phenyl system; indeed lithium biphenylide in THF converts alkyl chlorides into alkyllithium compounds² in preference to alkylation of biphenyl). In liquid ammonia carbanions are very readily protonated (at a rate exceeding migration of phenyl in 2,2,2-triphenylethyl anion¹⁶) whereas in THF organoalkali compounds are much longer lived such that the cyclization $\text{e} \rightarrow \text{d}$ may now occur, especially where the para substituent is phenyl rather than carboxylate. Scheme III ($\text{Z} = \text{Ph}$) also contains the likely intermediate(s) which, unlike 4-*p*-biphenylbutyllithium itself, cyclizes readily to give ultimately 8-phenylspiro[4.5]-6,8-decadienyllithium

(**7**) during reaction of lithium metal with 4-chloro-1-*p*-biphenylbutane in THF; we would suggest that **b** and **e** (prior to firm bonding to lithium cation) are possibilities for such an intermediate.

Experimental Section¹⁷

1-*p*-Biphenyl-1-butanone (mp 94–95°, lit.¹⁸ 94°) was prepared by a procedure similar to that of Kaplan et al.¹⁸ Reduction of 1-*p*-biphenyl-1-butanone by a modified Wolff-Kishner process¹⁹ in triethylene glycol gave 1-*p*-biphenylbutane (**9**) (bp 140–141° (3 Torr), lit.¹⁸ 140–141° (3 Torr)). 4-*p*-Biphenylbutanoic acid (mp 116–118° from isooctane, lit.²⁰ 118°) was prepared from biphenyl in an overall yield of 43% by the procedure of Weizmann, Bergmann, and Bograchov.²⁰ Methyl 4-*p*-biphenylbutanoate (bp 177° (0.2 Torr), lit.²¹ bp 212–215° (3 Torr)) was prepared by esterification of the acid with methanol (H_2SO_4). 2-*p*-Biphenylpentanenitrile (mp 82–83°, lit.²² 83°) was prepared from *p*-biphenylacetonitrile by a procedure similar to that of Cavallini et al.;²² hydrolysis of this nitrile gave 2-*p*-biphenylpentanoic acid (**10**): mp 113–115° (lit.²² 117°); NMR (CDCl_3) δ 0.94 (3 H, t, $J = 6$ Hz, CH_3), 1.36 (2 H, m, CH_2 at C-4), 1.96 (2 H, m, CH_2 at C-3), 3.63 (1 H, t, $J = 7$ Hz, CH at C-2), 7.3–7.7 (9 H, m, aromatic CH), 10.7 (1 H, broad s, CO_2H); mass spectrum m/e (rel intensity) 254 (65, M^+), 211 (8), 209 (9), 167 (100). Alkali metals and solvents were of the grade and purity previously specified.²

4-*p*-Biphenyl-1-butanol. A solution of 32.2 g (0.127 mol) of methyl 4-*p*-biphenylbutanoate in 30 ml of tetrahydrofuran (THF) was added over a period of 45 min to a stirred suspension of excess (28 g, 0.74 mol) of lithium aluminum hydride in 300 ml of THF at reflux under an atmosphere of nitrogen. Stirring was continued at reflux for 5 hr. After careful decomposition with water and ice-cold hydrochloric acid, the reaction mixture was extracted with ether; the ether extract was washed with 5% NaHCO_3 solution and then water, dried over anhydrous MgSO_4 , and filtered. After removal of solvent and recrystallization from CCl_4 , there was obtained 28 g (98% yield) of colorless plates: mp 72.0–73.0°; NMR (CDCl_3) δ 1.5–1.8 (5 H, m, CH_2CH_2 and OH), 2.66 (2 H, t, $J = 6.5$ Hz, ArCH_2), 3.63 (2 H, t, $J = 7$ Hz, CH_2O), 7.1–7.7 (9 H, m, aromatic CH).

Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}$: C, 84.91; H, 8.02. Found: C, 84.87; H, 8.07.

4-*p*-Biphenyl-1-butanol-1,1- d_2 . Addition of 34.0 g (0.127 mol) of methyl 4-*p*-biphenyl-1-butanoate in 50 ml of THF over a period of 30 min to 6.3 g (0.15 mol) of lithium aluminum deuteride in 350 ml of THF stirred at reflux temperature gave, after stirring another 5 hr at reflux and the usual work-up, 29 g of product, mp 55–62°. One recrystallization from CCl_4 gave 23 g (80% yield) of plates: mp 72.0–73.0°; NMR (CDCl_3) δ 1.5–1.8 (4 H, m), 2.07 (1 H, s, OH), 2.63 (2 H, t, $J = 6.5$), 3.6 (no H detectable), 7.1–7.7 (9 H, m).

4-*p*-Biphenyl-1-chlorobutane (**4h**). This compound was prepared from 4-*p*-biphenyl-1-butanol with thionyl chloride in pyridine by the procedure previously reported²³ for 2-phenylethyl-1- ^{14}C chloride. The product after distillation in vacuo was obtained in 64% yield as colorless liquid: bp 175° (0.07 Torr); NMR (CDCl_3) δ 1.75 (4 H, m, CH_2CH_2), 2.63 (2 H, t, $J = 7$ Hz, ArCH_2), 3.48 (2 H, t, $J = 7$ Hz, CH_2Cl), 7.1–7.8 (9 H, m, aromatic CH).

Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{Cl}$: C, 78.51; H, 7.00; Cl, 14.49. Found: C, 78.49; H, 7.07; Cl, 14.37.

4-*p*-Biphenyl-1-chlorobutane-1,1- d_2 (**4d**). This compound was prepared from 4-*p*-biphenyl-1-butanol-1,1- d_2 by the procedure described above for the protium compound: NMR (CDCl_3) δ 1.70 (4 H, m), 2.57 (2 H, t, $J = 7$ Hz), 3.5 (no H detectable), 7.0–7.7 (9 H, m).

General Procedure for Alkali Metal Reactions. All reactions with alkali metals were run under a nitrogen atmosphere in a Morton high-speed stirring apparatus according to the procedure given previously.^{2,4} For carbonylation and protonation of organoalkali products the reaction mixtures were forced under nitrogen pressure through a glass-wool filter on the end of the siphon tube to remove as much unreacted alkali metal as possible. All reactions with cesium and Cs-K-Na alloy were run with the usual Morton apparatus enclosed in a glove box under an atmosphere of nitrogen to reduce fire hazards.

Reactions of 4-*p*-Biphenyl-1-chlorobutane with Alkali Metals in Tetrahydrofuran. A. With Lithium. To 2.50 g (0.360 g-atom) of lithium wire cut into small pieces in 250 ml of tetrahydrofuran (THF) at -10° were added 1.0 ml (0.016 mole) of methyl iodide and 5% of a solution of 4.85 g (0.0198 mol) of 4-*p*-biphenyl-1-chlorobutane (**4h**). After 3 min of vigorous stirring a pink color appeared in the solution; after 7 min more of stirring the solution was cooled to -70° and the remainder of the chloride was added dropwise over a period of 54 min. After 40 min more of stirring at -70° , the solution suddenly changed from a dark red to a dark green color (probably due to formation of a little radical anion) and was immediately forced onto crushed solid carbon dioxide (i.e., "carbonated"). The residual contents of the reaction flask were decomposed with methanol; analysis of the resultant neutral materials by gas-liquid partition chromatography²⁴ (GLC) at 200° indicated the presence of 68 area % of 1-*p*-biphenylbutane (**9**) and 32% of 8-phenylspiro[4.5]deca-6,9-diene (**11**) at 0.65 times the retention time of **9**. The carbonated solution was allowed to stand overnight and then 100 ml of water was added. The THF was largely removed under partial vacuum, the aqueous residue was extracted with ether, and the ethereal solution was washed with water, dried over anhydrous MgSO_4 , and filtered. Removal of ether gave 0.94 g of neutral product which contained only hydrocarbon **9**, according to GLC analysis of its volatile constituents. The aqueous phase after acidification and the usual isolation procedure by extraction with ether gave 3.14 g of crude acids which upon analysis as methyl esters by GLC²⁴ at 191° were found to contain 37 area % of **12** and 63% of **8** at 2.6 times the retention time of **12**. A 1.99-g portion of the crude acids was distilled (in a sublimation apparatus) at $50\ \mu$ and a bath temp of 168° to give 1.76 g of product, mp $100-105^\circ$. A 0.506-g portion of the distillate after two recrystallizations from CS_2 gave 0.21 g of **8** as platelets: mp $127-128^\circ$; ν_{max} (95% EtOH) $253\ \text{nm}$ (ϵ 16,100); NMR (CDCl_3) δ 1.70 (4 H, m, CH_2 at C-3 and C-4), 2.39 (2 H, t, $J = 6\ \text{Hz}$, CH_2 at C-2), 2.68 (2 H, t, $J = 6\ \text{Hz}$, CH_2 at C-5), 7.1-7.7 (9 H, m, aromatic CH), 10.93 (1 H, broad s, CO_2H); mass spectrum molecular ion at m/e 254.

Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2$: C, 80.28; H, 7.13. Found: C, 80.52; H, 7.12.

From the above evidence and its mode of synthesis, compound **8** is assigned the structure of 5-*p*-biphenylpentanoic acid.

Removal of the solvent from the mother liquors which had yielded **8** gave a mixture of acids which was chromatographed on silica gel (70-325 mesh ASTM, E. Merck A.-G., Darmstadt, Germany, No. 7734) with elution by a 1:1 (by volume) mixture of *n*-hexane and benzene to give in early fractions 0.082 g of **8** and in later fractions 0.041 g of **12**. Compound **12** after recrystallization from *n*-heptane was obtained as colorless needles: mp $130-131^\circ$; ν_{max} (95% EtOH) in nm (ϵ) 253 (241), 257 (248), 259 (293), 262 (283), 264 (242), 269 (210); NMR (CDCl_3) δ 1.5-1.9 (8 H, m, aliphatic CH), 5.93 (4 H, AB quartet, $\Delta\nu = \delta 0.10$, $J = 11\ \text{Hz}$, vinylic CH), 7.30 (5 H, broad s, aromatic CH), 11.4 (1 H, broad s, CO_2H); mass spectrum m/e (rel intensity) 254 (2, M^+), 209 (82), 210 (37), 180 (20), 167 (100), 152 (14), 91 (12).

Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2$: C, 80.28; H, 7.13. Found: C, 80.03; H, 7.27.

From the above evidence and its mode of synthesis, compound **12** is assigned the structure of 8-phenylspiro[4.5]deca-6,9-diene-8-carboxylic acid.

The above reaction was repeated in detail but with reaction of 4-*p*-biphenyl-1-chlorobutane-1,1- d_2 (**4d**) (3.93 g, 0.0159 mol) and 1.55 g (0.223 g-atom) of lithium. After completion of the reaction at -70° , a small sample from the reaction mixture was decomposed with methanol and the remainder carbonated. Analysis of the products of methanolysis by GLC²⁴ indicated the presence of 25 area % of **11**, 65% of **9**, and 10% of an unknown at relative retention times of 0.65:1:1.48 respectively at 200° . From the carbonation there was isolated 0.62 g of neutral product and 2.98 g of crude acids. Analysis of the acids as methyl esters by GLC gave 35 area % of **12** and 65% of **8** at 2.2 times the retention time of **12** at 230° . A 1.16-g portion of the acid was recrystallized from CS_2 to give 0.32 g of purified acid: mp $127-128^\circ$; NMR (CDCl_3) δ 1.75 (4.1 H, m), 2.4 (no H in evidence), 2.72 (2.0 H, t, $J = 6\ \text{Hz}$), 7.1-7.7 (8.9 H, m), 10.92 (1.0 H, broad s). From the spectral evidence this acid appears to be entirely 5-*p*-biphenylpentanoic-2,2- d_2 acid.

In another reaction of **4h** (2.53 g, 0.0104 mol) with lithium (1.45 g, 0.209 g-atom) run in the THF at -70° as in the first run, as soon as the color of the reaction mixture changed to dark green, the solution was siphoned through a glass wool filter (to remove excess lithium metal) into a second flask under a nitrogen atmosphere. The solution was then allowed to stand at $-5 \pm 1^\circ$ for 3 hr before carbonation of the red solution. The usual work-up gave 0.85 g of ether soluble neutral product, 0.05 g of acid, and 0.8 g of a white solid (mp ca. $110-140^\circ$) which was insoluble in ether or alkali and is therefore thought to be a polymeric hydrocarbon. According to analysis by GLC the acid was essentially pure compound **12** while the volatile neutral material contained 13 area % **11**, 66% **9**, 3% **4h**, and 8 and 9% of two unknowns at 1.5 and 2.0 times the retention time of **9** at 200° . Recrystallization of the acid from CS_2 gave **12**, mp $129-130^\circ$.

B. With Potassium. To 250 ml of THF was added 1.67 g (0.0427 g-atom) of potassium and the mixture was heated under reflux with vigorous stirring for 1 hr. To the finely divided potassium was added 4.99 g (0.0204 mol) of **4h** in 40 ml of THF over a period of 5 min. Vigorous stirring at reflux was continued for 5 more min and then the dark reddish brown solution was allowed to cool toward room temperature for 20 min before forcing it onto a large excess of solid carbon dioxide. The residue in the flask was decomposed with methanol. Analysis of the methanolysis product by GLC²⁴ at 200° indicated the presence of 28 area % of **11**, 55% of **9**, and 17% of an unknown at 2.1 times the retention time of **9**. Solvent was removed from the carbonated mixture on a rotatory evaporator under vacuum, 200 ml of water was added (*Caution! Fire Hazard!*), and the solution was extracted with ether. The ethereal solution, after drying over anhydrous MgSO_4 , yielded 1.36 g of oily neutral product; analysis of this product by GLC at 200° gave 74 area % of **9** and 26% of the unknown product of 2.1 times the retention time of **9**. This unknown is likely 4-*p*-biphenyl-1-butene since its mass spectrum gave a molecular ion at m/e 208 as expected for $\text{C}_{16}\text{H}_{16}$. The aqueous phase after acidification with hydrochloric acid and extraction with ether yielded 2.70 g of crude acids. Analysis of the acids as methyl esters by GLC²⁴ revealed the presence of 76 area % of **12** and 24% of **10** at 1.5 times the retention time of **12** at 170° . The identity of **10** as 2-*p*-biphenylpentanoic acid was confirmed by comparison of its GLC retention time and mass spectrum with that of the authentic sample of this acid. A sample (1.0 g) of the crude acid was distilled in vacuo at a bath temperature of 150° at 0.6 Torr to give 0.62 g of a colorless viscous oil, which after one recrystallization from CCl_4 gave 0.32 g of crystals, mp $115-120^\circ$. One recrystallization of 0.10 g of this acid from *n*-pentane gave 0.07 g of crystals of mp $130-131^\circ$ as expected for 8-phenylspiro[4.5]deca-6,9-diene-8-carboxylic acid. This acid was further characterized by its NMR and mass spectrum.

The first run was repeated with a THF solution of 3.19 g (0.0130 mol) of **4h** added to 1.12 g (0.0287 g-atom) of potassium over a period of 2 min with stirring at reflux 3 min before cooling and carbonating. The usual work-up gave 1.09 g of neutral product and 1.76 g of crude acids. Quantitative GLC analysis²⁴ of the neutral material showed the presence of 0.25 g (9.0% yield) of **9**, 0.005 g (0.2% yield) of **11**, and 0.038 g of olefin; similar analysis of the acids as methyl esters gave 0.73 g (22% yield) of **12** and 0.18 g (5.5% yield) of **10**. Thus a considerable portion of both the acidic and neutral products were nonvolatile.

The first run was repeated in detail with 1.43 g (0.0366 g-atom) of potassium and 4.49 g (0.0183 mol) of **4d** except that, after the reaction mixture had been allowed to cool, the contents of the reaction flask were forced onto 250 ml of ice and water (the usual Morton apparatus was enclosed in a glove box under an atmosphere of nitrogen to prevent the hazard of fire during the hydrolysis). The usual isolation procedure gave 3.55 g of product which according to analysis by GLC contained 32 area % of **11**, 64% of **9**, and 4% of olefin. The crude product was separated by chromatography on neutral alumina with cyclohexane as eluent; the first fraction contained 0.21 g of **11**, the second a mixture of **11** and **9**, and the third 0.97 g of pure **9**. The isotopic distribution in **9** was determined from its mass spectrum which at m/e of 210-214 for the molecular ion corresponded to 97% d_2 , 2% d_1 , and 1.0% d_0 ($\pm 1\%$) components and at m/e 167-169 showed less than 1% d_2 component in the $\text{C}_{13}\text{H}_{11}^+$ ion fragment; accordingly the **9** isolated here was substantially pure 1-*p*-biphenylbutane-4,4- d_2 as was also demonstrated by its NMR spectrum (CDCl_3): δ 0.93 (0.9 H, t, $J = 5\ \text{Hz}$,

CD₂H), 1.1–1.9 (4.0 H, m, CH₂CH₂), 2.57 (2.1 H, t, *J* = 7 Hz, ArCH₂), 7.0–7.6 (9 H, m, aromatic CH).

C. With Cesium. In a run at 65°, 3.34 g (0.0204 g-atom) of cesium was stirred vigorously in 250 ml of THF for 1 hr at reflux; then to this mixture was added dropwise a solution of 2.88 g (0.0118 mol) of **4h** in 25 ml of THF over a period of 3 min with stirring continued for 2 min more before cooling over a period of 10 min and then carbonation. The usual work-up following addition of methanol to decompose any unreacted cesium gave 0.86 g of neutral material which according to quantitative GLC analysis²⁴ contained 1.25 mg (0.059%, based on cesium) of **11**, 45 mg (2.1%) of **9**, and nonvolatile material. The yield of crude acids was 1.90 g, which according to quantitative GLC analysis contained 0.70 g (27%) of **12** and 0.124 g (4.8%) of **10**.

In a repetition of the first run, after stirring the THF at reflux with cesium (3.05 g, 0.029 g-atom) for 1 hr, the mixture was cooled to 35° before addition of 2.56 g (0.0105 mol) of **4h** in 25 ml of THF dropwise over a period of 3 min with stirring continued for 3 min more and cooling for 5 min before carbonation. The usual work-up gave 0.50 g of neutral product which, by quantitative GLC, contained 1.9 mg (0.09% yield based on **4h**) of **11**, 70 mg (3.2%) of **9**, and some 9 mg of an unknown, likely 4-*p*-biphenyl-1-butene, of 2.1 times the retention time of **9** at 200°. The crude carboxylic acid amounted to 1.89 g and contained, according to quantitative GLC, 0.278 g (10.4%) of **10** and 1.58 g (59%) of **12**.

The previous runs at 35° were repeated with 5.85 g (0.0441 g-atom) of cesium and 5.33 g (0.0218 mol) of **4h**; after completion of the addition of the chloride and stirring for 3 more minutes, the dark green solution was cooled to –70° and 50 ml of methanol was added dropwise. The usual work-up gave 4.4 g of neutral product which according to quantitative GLC analysis²⁴ contained 0.25 g (5.4%) of **11**, 0.35 g (7.7%) of **9**, and no appreciable quantity of other products volatile under GLC conditions.

D. With Cs–K–Na Alloy. A mixture of 5.03 g (0.0378 g-atom) of cesium, 1.80 g (0.0460 g-atom) of potassium, 0.260 g (0.0113 g-atom) of sodium, and 250 ml of THF was stirred vigorously at reflux temperature for 1 hr. The solution was cooled to –70° with vigorous stirring continued while 1.033 g (0.00422 mol) of **4h** in 25 ml of THF was added dropwise over a period of 2 min. Stirring of the red solution was continued for 2 min more whereupon the solution turned green and was immediately carbonated. The usual work-up gave 0.023 g of neutral material and 1.02 g of crude acids. Analysis²⁴ of the neutral product by GLC indicated the presence of 94 area % of **9**, 4% of **11**, and 2% of an unknown; similar analysis of the acids as methyl esters gave 97 area % of **12** and 3% of **10**. The crude acid (0.83 g) was purified by chromatography on silica gel with elution by 95% (by vol) cyclohexane and 5% ether; the first component eluted, after recrystallization from a mixture of cyclohexane and heptane, consisted of 0.44 g of white needles of mp 130–131°. The spectral properties of the crystalline product were identical with those of other samples of **12**.

A second run was conducted just like the first with 4.62 g (0.0347 g-atom) of cesium, 1.80 g (0.0461 g-atom) of potassium, 0.200 g (0.0087 g-atom) of sodium, and 2.36 g (0.00964 mol) of **4h**. Carbonation and the usual work-up gave 0.28 g of neutral product which according to quantitative GLC contained 6.7 mg (0.33%) of **11**, 50 mg (2.5%) of **9**, and no appreciable additional volatile products under GLC conditions; in addition 2.02 g of acid was obtained which, according to quantitative GLC analysis of the methyl esters, consisted of 1.86 g (76%) of **12** and 0.109 g (4.5%) of **10**.

In a third run, conducted like the first run except as indicated, 5.43 g (0.0408 g-atom) of cesium, 1.94 g (0.0497 g-atom) of potassium, 0.281 g (0.0122 g-atom) of sodium, and 5.25 g (0.0214 mol) of **4h** were allowed to react at –70°. Three minutes following completion of the addition of **4h** to the alloy, the reaction mixture was forced into 200 ml of methanol chilled to –70°. The usual work-up gave 4.4 g of neutral product which according to analysis²⁴ by GLC contained 41 area % of **11**, 52% of **9**, and small quantities of two unknowns at 0.50 and 0.81 times the retention of **9** at 191°. The neutral product upon chromatography on neutral alumina with cyclohexane as eluent gave in a first fraction 0.20 g of **11** and in a subsequent fraction 0.21 g of **9**. Compound **11** had the following properties: NMR (CDCl₃) δ 1.5–1.8 (8 H, m, aliphatic CH), 3.92 (1 H, t, *J* = 1.5 Hz), 5.67 (4 H, ca. d, *J* = 1.5 Hz, vinyl-

ic CH), 7.25 (5 H, broad s, aromatic CH); mass spectrum *m/e* (rel intensity) 210 (63, M⁺), 168 (44), 167 (100), 155 (38), 91 (37).

Anal. Calcd for C₁₆H₁₈: C, 91.37; H, 8.63. Found: C, 91.25; H, 8.69.

From its recorded properties and mode of synthesis compound **11** is assigned the structure of 8-phenylspiro[4.5]deca-6,9-diene.

Various attempts were made to improve the yield of **11** from protonation of the THF solution of the organoalkali compounds. Thus the previous reaction was repeated and an aliquot was protonated with methanol at –70°. The remainder was warmed to –35° and then 20 g of mercury was added over a period of 10 min with stirring; the dark green solution returned to a dark red color (because of destruction of radical anions of biphenyl nuclei). An aliquot of the solution at –35° was protonated by addition to excess ice-water and another aliquot by addition to excess methanol at room temperature. The remainder of the solution was cooled to –70°, an aliquot was decomposed by addition to methanol at –70°, and the remainder was carbonated. Analysis of the four protonated aliquots by quantitative GLC indicated that the absolute yield of hydrocarbon **11** was uniformly low (6 ± 1%) although the yield of carboxylic acid from the final carbonation was high, indicative of a yield of at least 65% of the spiro anion **7**.

E. With Potassium in the Presence of Proton Donors. A mixture of 4.23 g (0.108 g-atom) of potassium in 250 ml of THF was stirred at reflux for 1 hr. Stirring was stopped while a solution of 52.7 g (0.71 mol) of *tert*-butyl alcohol, 0.957 g (0.00391 mol) of **4h**, and 25 ml of THF was added at one time. Stirring was soon started again and continued for 5 min at reflux. The solution was allowed to cool for 10 min and then carbonated. The carbonated solution was concentrated on a rotatory evaporator to 30 ml, water was added, and the solution was extracted with ether. The ethereal extract gave 0.9 g of crude neutral product which by quantitative GLC analysis²⁴ contained some 2% of **9** and 90% of a compound of 0.58 times the retention time of **9** at 189°. The crude product was purified by chromatography on neutral alumina with cyclohexane as eluent; the first fraction contained 0.75 g of colorless oil: bp 100–110° (0.9 Torr) (lit.²⁵ 111.8° (1.5 Torr)); NMR (CDCl₃) δ 0.83 (3.0 H, t, *J* = 7 Hz, CH₃), 1.0–2.0 (13.9 H, m, aliphatic CH), 2.53 (3.0 H, m or ca. t, *J* = 7 Hz, benzylic CH), 7.05 (4 H, m, aromatic CH); mass spectrum *m/e* (rel intensity) 216 (100, M⁺), 173 (71), 117 (61), 104 (40), 91 (60). On the basis of the data listed and its mode of synthesis, this compound is assigned the structure of 1-(*p*-cyclohexylphenyl)butane (**13**).

The first run was repeated but with addition of 1.24 g (0.0051 mol) of **4h** and 4.10 g (0.056 mol) of *tert*-butyl alcohol in 25 ml of THF to 0.444 g (0.0114 g-atom) of potassium in 250 ml of THF at reflux. Quantitative analysis of the product by GLC indicated the presence of 17 mol % of **13**, 11% of **9**, and 62% of unreacted **4h**.

The first run was repeated but with addition of 1.04 g (0.0042 mol) of **4d** and 52.8 g (0.71 mol) of *tert*-butyl alcohol to 4.25 g (0.109 g-atom) of potassium in 250 ml of THF at reflux. Distillation of the crude product in vacuo gave 0.82 g (90% yield) of colorless liquid, bp 110–115° (1.5 mm), which upon analysis by GLC showed only one peak at the retention time of 1-(*p*-cyclohexylphenyl)butane: NMR (neat) δ 0.91 (1.0 H), 1.0–2.0 (14 H), 2.54 (3.0 H), 7.03 (4.0 H). On the basis of the NMR spectrum, the product was 1-(*p*-cyclohexylphenyl)butane-4,4-*d*₂. A repetition of this run with **4d** but with 14.9 g (0.201 mol) of *tert*-butyl alcohol gave a product of the same structure and isotopic composition according to analysis by GLC and NMR.

The first run was repeated with addition of 2.13 g (0.00870 mol) of **4h** and 3.54 g (0.0305 mol) of 3-ethyl-3-pentanol in 25 ml of THF to 1.06 g (0.0271 mol) of potassium in 250 ml of THF at reflux. Analysis of the product by GLC and mass spectrometry gave the following products listed as absolute percent yield, relative retention time at 166°, *m/e* of molecular ion, identity: 27, 0.60, 216, **13**; 6, 0.66, 210, **11**; 9, 0.77, 214, likely 4'-*n*-butyl-1,2,3,4-tetrahydrobiphenyl; 9, 1.00, 210, **9**; 25, 1.10, 212, likely, 4'-*n*-butyl-1,4-dihydrobiphenyl; and 9% unreacted **4h**.

Reaction of 4-*p*-Biphenyl-1-chlorobutane with Alkali Metals in Dioxane. A. With Sodium. Purified dioxane (250 ml) was stirred at reflux in a Morton apparatus with potassium and then distilled into a second Morton flask immediately before use. To the dioxane was added 0.48 g (0.021 g-atom) of sodium and the mixture was stirred for one hour at reflux before a solution of 2.23 g (0.0091 mol) of **4h** in 25 ml of dioxane was added dropwise over a period of

5 min to the vigorously stirred, finely divided, molten sodium. The mixture was then stirred at reflux for 25 min and cooled to room temperature for 10 min before a 10-ml aliquot was decomposed with methanol and the remainder carbonated. The usual work-up of the carbonation mixture gave 1.69 g of neutral material and a negligible quantity of acids. Analysis of the product by GLC at 200° and mass spectrometry gave the following products listed as area percent yield (unless otherwise specified), relative retention time, *m/e* of molecular ion, identity: 1, 0.20, 168, likely *p*-methylbiphenyl; 1, 0.43, 182, likely *p*-ethylbiphenyl; 1, 0.61, 206, unknown; 62% absolute yield, 1.00, 210, 9; and 18% of unreacted 4h. The product from methanolysis was indistinguishable from that of carbonation.

The first run was repeated with 0.34 g (0.0148 g-atom) of sodium and 1.45 g (0.0059 mol) of 4d. There were isolated no carboxylic acids and 1.17 g of neutral product. The latter according to quantitative GLC analysis contained 58% of 9 and 26% of starting 4d. The neutral product upon column chromatography on alumina with cyclohexane as eluent gave a first fraction of 0.53 g of 9: NMR (CDCl₃) δ 0.92 (1.0 H, t, *J* = 5 Hz, CD₂H), 1.1–1.9 (4.0 H, m), 2.57 (2.1 H, t, *J* = 7 Hz, ArCH₂), 7.0–7.6 (9.0 H, m); mass spectrum *m/e* (rel intensity) 214 (1.6), 213 (17), 212 (88), 211 (1.2), 210 (0.2), 169 (1.8), 168 (17.1), 167 (100), 166 (4.6). These data show that 9 is essentially pure (>98%) 1-*p*-biphenylbutane-4,4-*d*₂.

B. With Potassium. Purified dioxane (250 ml) was stirred vigorously at reflux for 1 hr with 0.309 g (0.0077 g-atom) of potassium. A solution of 0.824 g (0.00334 mol) of 4d in 25 ml of dioxane was added dropwise over a period of 10 min. The light orange solution was stirred for another 20 min at reflux, cooled to room temperature for 15 min, and then carbonated. The usual work-up gave 0.73 g of neutral material and only a trace of acids. Quantitative analysis by GLC revealed the presence of 0.13 g (18% yield) of 11, 0.43 g (60%) of 9, and some 0.09 g of an unknown of 1.7 times the retention times of 9. A sample of 9 was separated by GLC and subjected to mass spectral analysis; the analysis confirmed the identity of 9 but showed that it was accompanied by likely a dihydro derivative (*m/e* 214). Since this impurity complicates interpretation of the cleavage fragment at *m/e* 167–169, it may be concluded only that 9 is >89% 1-*p*-biphenylbutane-4,4-*d*₂. In a similar run with 4h an 88% yield of neutral hydrocarbon and an 8% yield of crude acids were obtained; the hydrocarbons were similar to those obtained from 4d while the acids by quantitative GLC contained 1.7% (based on starting chloride) of 12 and 0.3% of 10.

NMR Spectrum of Spiro Anion 7. A. From 11 with Butyllithium. A 5-ml reaction vial containing a magnetic stirring bar and 1 ml of tetrahydrofuran-*d*₈ (from Novell Chemical Co., Inc.) was flushed with nitrogen and sealed with a rubber septum before addition by means of a hypodermic syringe of 0.5 ml of 12% *n*-butyllithium in heptane. The solution was stirred for 5 min at room temp and then 0.025 ml of 8-phenylspiro[4.5]deca-6,9-diene was added via syringe. The solution immediately developed a red color. After the solution had been stirred for 5 min more, a 0.5-ml portion was transferred via syringe to a nitrogen-filled NMR tube which was then tightly sealed. The NMR spectrum, measured at 40° relative to the nearest weak THF peak which was taken as δ 3.75 relative to TMS, consisted of signals at δ 4.24 (2 H, d, *J* = 9 Hz), 6.48 (2 H, d, *J* = 9 Hz), 6.7–6.9 (5 H, m, aromatic CH); the signals due to aliphatic protons were obscured by components of the solvent.

B. From 4h with Cs–K–Na Alloy. A 3-ml reaction vial containing a glass-enclosed (NOT Teflon!) magnetic stirring bar and 1 ml of THF-*d*₈ was flushed with nitrogen and sealed with a rubber septum. Some 0.3 ml of Cs–K–Na alloy (of the composition described earlier) was added and the reaction mixture was stirred for 2 hr at room temperature. The mixture was cooled to –70° and 0.025 ml of 4h was added via a syringe. The solution turned red and after 5 min of stirring it turned a dark green color. To this solution was

added via syringe some 0.3 ml of mercury. The solution was stirred for 3 min while cold and then was allowed to warm to room temperature with stirring. The final red solution was transferred with a syringe to a nitrogen-filled NMR tube which was then tightly sealed. The NMR spectrum, measured at 40° relative to solvent peak as previously described, consisted of signals at δ 1.49 (4 H, m, aliphatic CH), 1.69 (4 H, m, aliphatic CH), 4.43 (2 H, d, *J* = 9.5 Hz), 6.26 (2 H, d, *J* = 9.5 Hz), 6.6–6.9 (5 H, m).

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